

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2001-105400**

(43)Date of publication of application : **17.04.2001**

(51)Int.Cl.

**B81C 5/00**

**B23K 15/00**

**B23K 15/08**

**C25D 11/16**

(21)Application number : **11-344134**

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(22)Date of filing : **03.12.1999**

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(30)Priority

Priority number : **10368737**

Priority date : **25.12.1998**

Priority country : **JP**

**11047539**

**25.02.1999**

**JP**

**11216886**

**30.07.1999**

**JP**

**11216870**

**30.07.1999**

**JP**

**(54) METHOD OF MANUFACTURING FINE HOLES, FINE HOLES  
MANUFACTURED THEREBY AND STRUCTURAL BODY HAVING THE SAME**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide regularly-arranged fine holes excellent in linearity and to provide a manufacturing method for a structural body having the fine holes.

SOLUTION: This manufacturing method for fine holes and a nano structural body having the fine holes has a process for irradiating a particle beam onto a processed object, and a process for anodizing the processed object irradiated with the particle beam to form the fine holes in the processed object.

### LEGAL STATUS

[Date of request for examination]

15.11.2006

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision  
of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the nano structure and the nano structure which have available pore in the large range especially as functional materials, such as an electron device, and an optical device, a micro device, a structural material, etc. about the structure which has the pore and this pore which were manufactured by the manufacture approach of pore, and the list by this manufacture approach.

[0002]

[Description of the Prior Art] In a metal and the thin film of a semi-conductor, a thin line, and a dot, there is a unique thing for which electric, optical, and chemical property are shown by shutting up a motion of an electron in size smaller than a certain characteristic die length. The interest about the ingredient (nano structure) which has structure more detailed than several 100nm as high-performance material from such a viewpoint is increasing.

[0003] As the manufacture approach of such the nano structure, photolithography is begun and the method of manufacturing the nano structure directly with semi-conductor processing techniques including detailed pattern formation techniques, such as electron beam lithography and X-ray lithography, is mentioned, for example.

[0004] Moreover, the attempt which is going to realize the new nano structure is in the base in the regular structure formed automatically, i.e., the structure formed in a self-regulation target, besides such a manufacture approach. Since such technique may be able to manufacture the detailed and special structure which turns around the conventional approach a top depending on the fine structure used as the base, many researches are beginning to be done.

[0005] The anodic oxidation which can manufacture easily the nano structure which has the pore of nano size with sufficient control as such self-regular technique is mentioned. For example, the anodic oxidation alumina which manufactures aluminum and its alloy by anodizing in an acidic bath is known.

[0006] If aluminum plate is anodized in an acid electrolyte, a porosity oxide film will be formed (for example, reference, such as R.C.Furneaux, W.R.Rigby&A.P.Davids, "NATURE", Vol.337, and P147 (1989)). The very detailed cylindrical pore (nano hole) whose diameter is several nm - hundreds of nm has the description of this porosity oxide film in having the specific geometric structure of arranging in parallel at intervals of several nm - hundreds of nm (cell size). The pore of the shape of this cylinder has a high aspect ratio, and is excellent also in the uniformity of the path of a cross section. Moreover, when the path and spacing of this pore adjust the current in the case of anodic oxidation, and an electrical potential difference, the thickness of an oxide film and the depth of pore are controlling the time amount of anodic oxidation, and a certain amount of control is possible for them.

[0007] Moreover, the method of performing two steps of anodic oxidation, in order to improve the perpendicularity, the linearity, and the independence of pore, Namely, once removing the porosity oxide film anodized and formed, it anodizes again. The method of manufacturing the pore which shows better perpendicularity, linearity, and an independence is proposed ("Jpn.Journal of Applied Physics" , Vol.35, Part2, No.1B, pp.L126-L129, 1 January15, 996 issue). Here, this approach uses that the hollow of the front face of the aluminum plate made when removing the anodic oxide film formed by the first anodic oxidation serves as a pore formation start point of the 2nd anodic oxidation.

[0008] Furthermore, it anodizes, after forming the hollow which forces the approach of using a stamper and forming a pore formation start point in order to improve the controllability of the configuration of pore, spacing, and a pattern, i.e., the substrate which equipped the front face with two or more projections, on the surface of an aluminum plate, and can do it as a pore formation start point, and the method of manufacturing the pore which shows the controllability of a better configuration, spacing, and a pattern is also proposed (JP,10-121292,A).

[0009] Various application which paid its attention to the specific geometrical structure of this anodic oxidation alumina is tried. Although the description by Masuda is detailed, an application is listed hereafter. For example, there are application as a coat using the abrasion resistance of an oxide film on anode and insulation-proof and application of fill TAHE which exfoliates a coat. Furthermore, various application including coloring, a magnetic-recording medium, EL light emitting device, an electrochromic element, an optical element, a solar battery, and a gas sensor is tried from using the technique filled up with a metal, a semi-conductor, etc. in a nano hole, and the replica technique of a nano hole. Furthermore, the application to the directions of many, such as the quantum effectiveness devices, such as quantum wire and an MIM component, and a molecule sensor using a nano hole as a chemical reaction place, is expected (Masuda" solid-state physics", 31,493 (1996)).

[0010]

[Problem(s) to be Solved by the Invention] The manufacture approach of the direct nano structure by the semi-conductor processing technique expressed previously and pore has problems, like the badness of the yield and the cost of equipment are high, and technique which can be manufactured with sufficient repeatability by simple technique is desired.

[0011] Since the technique of anodic oxidation from such a viewpoint can manufacture the nano structure and pore with sufficient control comparatively easily, it is desirable.

[0012] However, although many techniques in which the pore object manufactured only by the usual anodic oxidation controlled the configuration of the pore and a pattern were developed, there was a limitation in the control. As control in anodic oxidation, the thing controllable to some extent is known [ depth / of pore / pole diameter ] for time amount in pore spacing on the anodic oxidation electrical potential difference at pore wide processing. Furthermore, the example which manufactured the regulation-ized nano hole arranged in the shape of a honeycomb by anodizing under suitable anodic oxidation conditions by Masuda and others as an example which controlled the array of pore is reported. However, in this regulation-ized nano hole, there were technical problems, like there is a limit to be anodized [ of long duration ] in spacing of the pore which can be manufactured.

[0013] Moreover, in the approach of performing two steps of anodic oxidation, although the perpendicularity, the rectilinear-propagation nature, and the independence of pore have improved and the good parts of spacing of pore and the controllability of a pattern also existed still more nearly locally, when seen on the whole, spacing and the pattern of pore had the technical

problem that these controllabilities were not good rather than were fixed.

[0014] In the approach of furthermore forming a pore formation start point using a stamper, the controllability of the configuration of pore, spacing, and a pattern had the technical problem which is described below, although improved.

(1) Since the stamper is used, it is difficult to form a pore formation start point in a front face to an irregular workpiece at homogeneity.

(2) Since there is risk of a workpiece being destroyed to the workpiece whose mechanical strength is not strong since it is necessary to put a pressure on a workpiece at the time of stamper use, application is difficult.

[0015] (3) Since it is difficult to expose aluminum on a front face to a workpiece by which the film was formed in the aluminum front face since compression by the stamper is used, it is difficult to make a stamp location into a pore formation start point.

(4) It is not easy to have to use a hydraulic press at the time of use of a stamper, and to position a pattern with high precision.

(5) It is not easy for manufacture of a stamper to manufacture without a defect the stamper which must use ultra-fine processing technology time-consuming [ like electron beam lithography ], and has the projection of uniform high density for a short time.

[0016] The purpose of this invention is to solve these technical problems. That is, the purpose of this invention is offering the technique which controls the configuration of pore, spacing, a pattern, a location, a direction, etc. in the structure which has the pore and pore which are manufactured by anodic oxidation.

[0017] It is providing coincidence with the technique which can be manufactured in a short time easily possible [ highly precise control of a pattern location ], without receiving constraint of existence of the film of the gestalt of a workpiece, for example, surface irregularity, a mechanical strength, and a front face etc. in this invention.

[0018] It is using as the base the nano structure which has the pore furthermore manufactured with the application of this technique, indicating the new nano structure and a nano structure device, and making use possible for a nano hole in directions various as a functional material.

[0019]

[Means for Solving the Problem] Then, the manufacture approach of the pore of this invention is characterized by having the process which irradiates a corpuscular ray at a workpiece, and the process which forms pore more at said workpiece for anodizing the workpiece which irradiated said corpuscular ray.

[0020] This invention is characterized also by said corpuscular ray being a charged particle beam again. Moreover, said corpuscular ray is characterized also by being a focused ion beam or an electron beam.

[0021] This invention is characterized by being the process which removes said film alternatively again by irradiating said corpuscular ray at the film with which the process which irradiates said corpuscular ray controls the anodic oxidation arranged on the front face of said workpiece.

[0022] This invention is characterized by being the process which forms in the front face of said workpiece alternatively the film which controls anodic oxidation again from the raw material contained in the ambient atmosphere in which the processes which irradiate said corpuscular ray surround said workpiece.

[0023] According to this invention, pore can be formed in the location of said pore formation start point by irradiating a corpuscular ray at a workpiece, and being able to form a pore

formation start point in a desired location, consequently anodizing a workpiece. For this reason, according to this invention, control of the array of the pore of the structure of a nano meter scale, spacing, a location, a direction, etc. is possible.

[0024] the workpiece which has irregularity in a front face since the manufacture approach of this invention uses the exposure of a corpuscular ray for formation of a pore formation start point at coincidence -- also receiving -- a pore formation start point -- homogeneity -- forming highly is easy.

[0025] Moreover, since it does not need to put a pressure on a workpiece when forming a pore formation start point, since the manufacture approach of this invention uses the exposure of a corpuscular ray for formation of a pore formation start point, a mechanical strength can apply it also to the workpiece which is not strong.

[0026] Moreover, even when the film is formed in a workpiece front face, the manufacture approach of this invention is irradiating a corpuscular ray at said film, and said film is removed partially and it can form a pore formation start point.

[0027] Moreover, since the manufacture approach of this invention uses corpuscular ray irradiation equipment, it is easy the approach to position a pattern with high precision using an attached secondary electron image observation function etc.

[0028] Furthermore, since the manufacture approach of this invention uses corpuscular ray irradiation equipment, it can form a pore formation start point by straight-writing. Therefore, the process resist spreading required for stamper manufacture etc., electron beam exposure, and time-consuming [ like resist removal ] is unnecessary, and it is possible to form a pore formation start point for a short time.

[0029]

[Embodiment of the Invention] Hereafter, the manufacture approach of the structure which has the pore of this invention and pore is mainly explained using drawing 1 . Drawing 1 is process drawing showing an example of the manufacture approach of the nano structure of this invention. Following process (a) - (c) mainly corresponds to (a) - (c) of drawing 1 .

[0030] (a) Prepare the workpiece 1 which forms preparation \*\*\*\* of a workpiece, and pore. Although the member which uses aluminum as a principal component is mentioned as a what workpiece this invention can be desirable and can apply, if it is the quality of the material in which the pore formation by anodic oxidation is possible, it will not be limited especially. For example, the member which uses Si, InP, or GaAs as a principal component can be used as a workpiece of this invention.

[0031] The example of the gestalt of the workpiece which this invention can be desirable and can apply is shown in (a) - (d) of drawing 3 . The bulk 11 which uses aluminum as shown in drawing 3 (a) as a principal component as an example of the 1st gestalt is mentioned. Moreover, in the bulk 11 which uses aluminum as a principal component, in order to give smooth nature to a front face, even if it is not necessarily required to perform mirror-polishing processing and some surface irregularity exists, this invention is applicable.

[0032] Next, what formed the film 12 which uses aluminum as a principal component on the base 13 as shown in (b) of drawing 3 as an example of the 2nd gestalt is mentioned. At this time, the thing in which the film of one or more layers was formed on substrates, such as insulator substrates and silicon including quartz glass, and semi-conductor substrates including gallium arsenide, and these substrates is mentioned as a base 13. However, if there is no un-arranging in the pore formation by anodic oxidation of the film 12 which uses aluminum as a principal component, the quality of the material of a base 13, thickness, especially a mechanical strength,

etc. will not be limited. For example, if what formed the film of pore formation terminal point members, such as Ti and Nb, on the substrate as a base 13 is used, it will also become possible to raise the homogeneity of the depth of pore. Moreover, as for the membrane formation approach of the film 12 which carries out a principal component, the membrane formation approach of arbitration including resistance heating vacuum evaporation, EB vacuum evaporation, a spatter, and CVD can apply aluminum. Moreover, in the film 12 which uses aluminum as a principal component, even if the surface irregularity resulting from existence of a grain etc. exists, this invention is applicable.

[0033] Next, what formed the membrane surface 14 in the thing ( drawing 3 (c)) which formed the membrane surface 14 in the bulk 11 which uses aluminum as a principal component as an example of the 3rd gestalt, or the thing which formed in base top 13 the film 12 which uses aluminum as a principal component ( drawing 3 (d)) is mentioned. Although an insulator, bulb metals (Nb, Ti, Ta, Zr, Hf, etc.), or C is mentioned, for example, if it is the quality of the material which is not inconvenient to the pore formation by anodic oxidation as the quality of the material of the membrane surface 14 formed in a front face at this time, it will not be limited especially.

[0034] Moreover, although not only the film of a monolayer but the film more than two-layer is mentioned as a membrane surface 14, if there is no un-arranging in the pore formation by anodic oxidation, neither the quality of the material of each layer nor especially its combination will be limited. For example, as shown in drawing 8 (a), in the case of the workpiece which is the two-layer film which is the conductive film 17 which the membrane surface 14 formed the insulator film 18 and on it, the manufactured nano structure becomes like drawing 8 (c), but it also becomes possible to apply the nano structure manufactured by using the conductive film on the top face of the maximum as a microelectronic device. Moreover, in a membrane surface 14, even if the surface irregularity resulting from existence of a grain etc. exists, this invention is applicable.

[0035] Although what has what [ not only / tabular ] is smooth as a configuration of the workpiece of this invention but a curved surface, the thing which has a certain amount of irregularity and level difference on a front face are mentioned, if there is no un-arranging in the pore formation by anodic oxidation, it will not be limited especially.

[0036] (b) It is irradiating a corpuscular ray 10 (their being a focused ion beam and an electron beam as a concrete example) at the formation process above-mentioned workpiece 1 of a pore formation start point, and form the pore formation start point 2 in a desired location.

[0037] A setup of the exposure location of the corpuscular ray to a workpiece can be carried out by being easily highly precise by using the observation means attached to corpuscular ray irradiation equipment.

[0038] The method of detecting the secondary electron generated especially as this observation means when corpuscular rays, such as a focused ion beam and an electron beam, are scanned on a sample, and obtaining a scan image is mentioned. By this approach, a corpuscular ray will be irradiated at a workpiece at the time of observation. However, it is possible for the effect of the particle radiation at the time of setting up the patterning location of a workpiece to be substantially disregarded by obtaining a scan image using the corpuscular ray of an amount small enough.

[0039] The approach of scanning the corpuscular ray itself and moving an exposure location as an approach of moving the exposure location of a corpuscular ray, the method of moving a workpiece, or the approach of combining the both is mentioned. Although the method of moving the corpuscular ray itself here is rational in equipment, since a movable distance has a limit, it is

thought that the approach of combining both is suitable to form a pore formation start point in a large area and high density. Moreover, if the sample stage in which highly precise position control is possible also about the approach of moving a workpiece is used, it is possible to apply this invention.

[0040] Next, the example of the formation approach of the pore formation start point by the particle radiation of this invention is explained using drawing 4 , drawing 10 , and drawing 11 . At this time, drawing 4 (a), drawing 4 (c), drawing 10 (a), drawing 10 (c), and drawing 11 (a) are the examples which formed the pore formation start point in the shape of a honeycomb mostly. Moreover, drawing 4 (b), drawing 4 (d), drawing 10 (b), drawing 10 (d), and drawing 11 (b) are the examples which formed the pore formation start point in the shape of forward 4 square shape mostly. Although various examples can be considered besides the example shown here, if there is no un-arranging in the pore formation by anodic oxidation, it will not be limited especially.

[0041] When it roughly divides, there are the following three approaches among the formation approaches of the pore formation start point by the particle radiation of this invention. a primary method is irradiating a corpuscular ray on a workpiece front face, and is physical in a workpiece front face -- and -- or it is the approach of making it changing chemically.

[0042] And the second approach is the approach of removing a mask partially by irradiating a corpuscular ray on the mask (film which controls anodic oxidation) formed in the workpiece front face, making expose the front face of a workpiece partially, and making that a pore formation start point.

[0043] Furthermore, the third approach is irradiating a corpuscular ray on a workpiece front face, and is the approach of forming in a workpiece front face a mask (film which controls anodic oxidation) around a part making into a pore formation start point from the raw material which exists in the ambient atmosphere which surround a workpiece.

[0044] First, a primary method is explained. There are an approach of irradiating a corpuscular ray alternatively only in a location making into a pore formation start point and the approach of forming a pore formation start point with the difference of the exposure, although a corpuscular ray is irradiated besides a location to make into a pore formation start point at a primary method.

[0045] It is the approach ( drawing 4 (a), (b)) of irradiating a corpuscular ray only in a location making into the above and a pore formation start point as an example of the approach of irradiating a corpuscular ray alternatively at a workpiece at the field of plurality [ shape / of a dot (circle) ], for example. By the approach shown in drawing 4 (a) and (b), after making a corpuscular ray stay at a certain dot location 31, it repeats moving to the dot location 31 of a degree and making a corpuscular ray stay, and it is performed. A pore formation start point can be formed in the field to which the corpuscular ray was irradiated by doing in this way. It is possible by shortening transit time between dots very much compared with the residence time in a dot location to lose substantially the effect of the particle radiation in the case of migration between dots to stop a corpuscular ray here at the time of migration between dots.

[0046] moreover -- as the example of the approach of forming a pore formation start point with the difference of the exposure of the above-mentioned corpuscular ray -- a workpiece -- a corpuscular ray -- the shape of Rhine -- and there is the approach ( drawing 4 (c), (d)) of irradiating so that an intersection may be formed. This approach is irradiating a corpuscular ray in the shape of Rhine in the different direction at a workpiece, and forms at least the part (intersection) irradiated twice. As shown in drawing 4 (c) and (d), the approach of scanning a corpuscular ray in the shape of [ which intersects perpendicularly mutually ] Rhine 32, and irradiating it only once is more specifically mentioned. In this approach, since the multiple-times

exposure of the corpuscular ray is carried out compared with that perimeter on the intersection 33 of Rhine, a pore formation start point can be formed in the intersection 33 of Rhine.

[0047] Here, why the part which irradiated the corpuscular ray, or a part with many corpuscular ray exposures (count) becomes a pore formation start point is explained below. chemical change (presentation change etc.) according to an ion implantation when a focused ion beam is used as a corpuscular ray -- and -- or it is presumed that the condition of differing from a perimeter is formed in a workpiece front face, the singular point at the time of it being anodic oxidation (pore formation start point) comes, and anodic oxidation advances by physical change by ion etching.

[0048] Moreover, as a corpuscular ray, when an electron ray is used, the physical conditions of changing, having reached or differing from a perimeter by chemical change (presentation change etc.), such as thermal deformation by electron beam exposure, damage generating, and evaporation, were formed in the workpiece front face, the singular point at the time of it being anodic oxidation (pore formation start point) came, and it is presumed that anodic oxidation advances.

[0049] The above-mentioned manufacture approach is irradiating a corpuscular ray on the surface of a workpiece, and makes directly the part which produced and cheated out of a certain change a pore formation start point at a workpiece. However, the formation approach of the pore formation start point of this invention is not restricted to the above-mentioned approach.

[0050] Next, the second approach of above mentioned this invention is explained. This approach arranges beforehand the film (membrane surface) 14 which controls anodic oxidation on the surface of a workpiece, as shown in drawing 3 (c), drawing 3 (d), or drawing 8 (a), a corpuscular ray is irradiated, by this, the above-mentioned film is partially removed only in the location of a request of this film, and the front face of a workpiece is exposed in it ( drawing 8 (b), drawing 11 (a), (b)). Let the front face of the exposed workpiece be a pore formation start point by this approach. As an example of the approach of irradiating a corpuscular ray only in a location making into the above and a pore formation start point, the approach ( drawing 11 (a), (b)) of irradiating a corpuscular ray in the shape of a dot (circle) is mentioned to a workpiece, for example. By the approach shown in drawing 11 (a) and (b), after making a corpuscular ray stay at a certain dot location 37, it repeats moving to the dot location 37 of a degree and making a corpuscular ray stay, and it is performed. The field which removed the membrane surface 14 of the field where the corpuscular ray was irradiated, was made to expose processing-ed, and was exposed by doing in this way can be made into a pore formation start point. It is possible by shortening transit time between dots very much compared with the residence time in a dot location to lose substantially the effect of the particle radiation in the case of migration between dots to stop a corpuscular ray here at the time of migration between dots.

[0051] Next, the third approach of above mentioned this invention is explained. Contrary to the second approach of the above, this approach can arrange the film 14 which controls the anodic oxidation described above on the surface of the workpiece only in a desired location by irradiating a corpuscular ray to the field of a request of a workpiece in the ambient atmosphere 7 containing the raw material for forming the film which controls anodic oxidation, as shown in drawing 9 (b). And as a result, the front face (front face of a workpiece in which the film 14 is not formed) of the workpiece which is not irradiating the corpuscular ray can be made into a pore formation start point ( drawing 10 ). as an example of the formation approach of the pore formation start point by this approach, a pore formation start point can be formed by leaving a pattern ( drawing 10 (a) and (b) -- the shape of a dot (circle), and drawing 10 (c) -- \*\*\*\* -- the shape of a rectangle) making into a pore formation start point, and irradiating the front face 35 of



the workpiece which remains with a corpuscular ray (d). Especially, it is drawing 10 (c) (d), In the shown pattern, a corpuscular ray can be scanned in the shape of Rhine on a workpiece front face, and the field 38 surrounded by the film which controls anodic oxidation can be made into a pore formation start point by placing the film which controls Rhine-like anodic oxidation and arranging spacing. Therefore, since a pore formation start point can be formed simply, it is desirable.

[0052] As film which controls the above-mentioned anodic oxidation, although an insulator is mentioned, for example, if it is the ingredient which can control anodic oxidation of a workpiece, a conductor or a semi-conductor will also be available. However, \*\* with desirable removing noble metals, in using a conductor in order to anodize to stability.

[0053] Why the non-irradiating location of the corpuscular ray in the inside of the ambient atmosphere containing the raw material for forming the film which controls anodic oxidation here becomes a pore formation start point is explained. In a particle-radiation location, the film is formed for the above-mentioned raw material on the workpiece of a particle-radiation location of a pyrolysis etc. And since the pore formation to the workpiece which exists directly under the film is controlled with the formed film, it is presumed that formation (growth) of the pore in corpuscular ray a non-irradiating location advances.

[0054] The ingredient which has a metal as a component is mentioned as the 1st mode of the class of raw material for forming the film which controls the above-mentioned anodic oxidation. for example, -- W -- (-- CO --) -- six -- Mo -- (-- CO --) -- six -- like -- a metal carbonyl -- metallurgy -- a group -- an organic compound -- SiCl -- four -- TiCl -- four -- ZrCl -- four -- TaCl -- four -- MoCl -- five -- WF -- six -- etc. -- a metal -- a halogenide -- or -- SiH -- four -- Si -- two -- H -- six etc. -- the gas of metal hydride [ like ] is mentioned.

[0055] Moreover, as the 2nd mode of the class of raw material for forming the film which controls the above-mentioned anodic oxidation, the gas of an organic compound which does not contain a metal as a component is mentioned. For example, gas, such as ketones, such as hydrocarbon compounds, such as aromatic compounds, such as a pyrene and torr nitril, methane, and ethane, and an acetone, is mentioned. However, if there is no un-arranging in the pore formation by anodic oxidation, especially the class of gas for membrane surface formation will not be restricted.

[0056] using independently as a usage of the raw material for forming the film which controls the above-mentioned anodic oxidation, and Ar, helium and N<sub>2</sub> etc. -- although mixing with gas and using etc. is mentioned, especially if there is no un-arranging in the pore formation by anodic oxidation, it will not be limited to these. [ moreover, ]

[0057] When the 1st raw material furthermore mentioned above is used, the film 14 which controls the above-mentioned anodic oxidation contains a metal. W (CO) When 6 is used as a raw material, the film containing W is formed. On the other hand, the film 14 which controls the above-mentioned anodic oxidation when the 2nd above-mentioned raw material is used turns into film containing carbon. However, in these film, other elements in an ambient atmosphere may be contained as an impurity.

[0058] Furthermore, as the above-mentioned raw material, in aluminum (CH<sub>3</sub>)<sub>3</sub> and the ambient atmosphere 7 containing AlCl<sub>3</sub>, aluminum film is formed on the surface of a workpiece, and concavo-convex aluminum is substantially formed in the field of a request of the workpiece which uses aluminum as a principal component by irradiating a corpuscular ray. Therefore, the crevice (the field which is not irradiating the corpuscular ray, or field with few exposures of a corpuscular ray) of aluminum can also be made into a pore formation start point. Therefore, it

can be considered that aluminum film acts in this case as film which controls anodic oxidation substantially.

[0059] Next, the corpuscular ray used for this invention is explained. When using a focused ion beam as a corpuscular ray in this invention, as the ion kind, Ga, Si, germanium, Cs, Nb, Cu, etc. which are the liquid metal ion source, O, N, H, helium, Ar which are a source of field ionization gas ion, etc. are mentioned. However, if there is no un-arranging in the pore formation by anodization, especially the ion kind of a focused ion beam will not be restricted.

[0060] However, it is desirable to use Ga as an ion kind of a focused ion beam from the reason of the ease of dealing with it etc. in the ease of treating in fact. Moreover, if the effectiveness of an ion implantation is taken into consideration, an element like noble metals which is hard to anodize may not be desirable as an ion kind of the focused ion beam in this invention. However, in for performing physical deformation of workpiece front faces, such as ion etching on the front face of a workpiece, it is not the limitation in order to form the film 14 for controlling the anodic oxidation mentioned above. Moreover, although it changes according to process terms and conditions, such as an ion kind and acceleration voltage, about the effectiveness by the ion implantation, it is desirable for the element of the ion kind more than lppm to exist in the pore formation start point.

[0061] on the other hand -- this invention -- when using an electron beam as a corpuscular ray to kick, it is desirable as the energy to use 1 or more keVs the thing of less than 10 MeV. Therefore, as electronic acceleration voltage, a several kV - about several MV thing is mentioned. However, if there is no un-arranging in the pore formation by anodization, especially the energy and acceleration voltage of an electron beam will not be restricted. However, it is desirable to use 10 or more keVs the thing of 1 or less MeV as energy of an electron beam from the reasons of the repeatability of the configuration of pore etc. in fact. Therefore, 10kV or more 1MV or less is desirable also as acceleration voltage of an electron beam.

[0062] Next, the arrangement pattern of a pore formation start point is explained. It is possible to form a pore formation start point in the location of arbitration in this invention. Moreover, it is not limited especially about spacing and the pattern of a pore formation start point location. However, when actual application is taken into consideration, it will form so that it may become the repeat of the almost same spacing and a pattern by being required to form in the location of the repeat of the almost same spacing and a pattern the nano structure which has pore and pore about a pore formation start point in that case.

[0063] At this time, since there is an inclination for the pattern of pore to become the repeat of a honeycomb-like pattern mostly by self-organizing when the member which uses aluminum as a principal component as a workpiece in the pore formation by anodic oxidation is used, it is desirable to form so that a pore formation start point may become the repeat of a honeycomb-like pattern mostly beforehand. This is desirable especially when it is going to form the structure which has deep pore. However, since the above-mentioned self-organizing does not happen yet when pore is shallow, it is also possible to form so that a pore formation start point may become the repeat of the pattern of configurations of arbitration, such as the shape of a square, mostly.

[0064] Moreover, in the pore formation by anodic oxidation, spacing of pore is controllable by process terms and conditions, such as the class of electrolytic solution used for anodic oxidation, concentration, temperature and the anodic oxidation electrical-potential-difference impression approach, an electrical-potential-difference value, and time amount, to some extent. Therefore, it is desirable to form a pore formation start point in spacing of the pore expected from process terms and conditions beforehand. For example, it is [0065] experientially between spacing 2R

(nm) and the anodic oxidation electrical potential differences  $V_a$  (Volt) of pore.

[Equation 1]

$$2R = 10 + 2V_a \quad (\text{式 } 1)$$

[0066] since there is \*\*\*\*\* -- the maximum access distance (spacing) 2 of a pore formation start point -- as the conditions for  $R_v$  (nm) and the anodic oxidation electrical potential difference  $V_a$  (Volt) -- [0067]

[Equation 2]

$$V_a = (2R_v - 10) / 2 \quad (\text{式 } 2)$$

[0068] It is desirable to apply \*\*\*\*\* conditions, especially the conditions with which a formula 2 is filled in \*\*30% of error range from a formula 2.

[0069] This is desirable especially when it is going to form the structure which has deep pore and deep pore. On the other hand, when the depth of the pore of the workpiece which it is going to form is shallow, the constraint specified from the above-mentioned conditions etc. about spacing of a pore formation start point becomes loose.

[0070] As mentioned above, especially spacing ( $2R_v$ ) of the pore formation start point by this invention is not restricted, but when actual application is taken into consideration, 5nm or more 1000nm or less is desirable.

[0071] Moreover, the intensity distribution of the corpuscular ray which can be used by this invention and which was mentioned above are carrying out Gaussian distribution mostly. therefore -- \*\*\*\* -- the particle-radiation field (namely, diameter of a corpuscular ray) which it can say and is irradiated to each pore formation start point has a desirable method of not lapping with the particle-radiation field (namely, diameter of a corpuscular ray) which irradiates the next pore formation start point. Therefore, as a diameter of the corpuscular ray used for processing in this invention, it is desirable that it is below spacing of a pore formation start point. Therefore, as a diameter of the corpuscular ray used for processing, a thing 500nm or less is desirable.

[0072] (c) Manufacture the structure which has pore 3 in the pore formation start point 2 by performing anodizing to the workpiece 1 in which the pore formation process above-mentioned pore formation start point was formed.

[0073] The outline of the anodic oxidation equipment used for this process is shown in drawing 5. It is the ammeter with which one measures a workpiece and the power source to which in a constant temperature bath and 42 the electrolytic solution and 44 impress a reaction container, and, as for 45, the cathode of Pt plate and 43 impress [ 41 ] an anodic oxidation electrical potential difference among drawing 5, and 46 measures an anodic oxidation current. Although omitted by a diagram, automatic control, the computer to measure are incorporated in the electrical potential difference and the current.

[0074] A workpiece 1 and a cathode 42 are arranged in the electrolytic solution kept constant in temperature with the constant temperature bath, and anodic oxidation is performed by impressing an electrical potential difference between a sample and a cathode from a power source.

[0075] Although oxalic acid, phosphoric acid, a sulfuric acid, a chromic-acid solution, etc. are mentioned, the electrolytic solution used for anodic oxidation will not be limited especially if there is no un-arranging in the pore formation by anodic oxidation. Moreover, terms and conditions according to each electrolytic solution, such as an anodic oxidation electrical potential difference and temperature, can be suitably set up according to the nano structure to manufacture.

[0076] By pore wide processing in which the above-mentioned nano structure is furthermore

dipped into an acid solution (the case of an anodic oxidation alumina for example, phosphoric-acid solution), a pore diameter can be extended suitably. It can consider as the structure which has the pore of a desired path with acid concentration, the processing time, temperature, etc.

[0077] An example (anodic oxidation alumina) of the configuration of the structure which has the pore of this invention is described in <configuration of the nano structure> drawing 2. A sectional view [ in / drawing 2 (a) and / in drawing 2 (b) / AA line of drawing 2 (a) ] is shown. [ a top view ] As for a workpiece and 3, in drawing 2, 1 is [ pore (nano hole) and 4 ] barrier layers.

[0078] The structure of this invention is explained here. this structure -- the cylinder-like pore 3 -- having -- each pore 3 -- mutual -- parallel -- and it arranges at equal intervals mostly. Several nm - hundreds of nm and spacing (cell size)  $2R$  of diameter  $2r$  of pore 3 are several nm - about hundreds of nm. the concentration of the electrolytic solution which uses spacing of pore 3, and a diameter for the formation conditions of a pore formation start point, or anodic oxidation, temperature and the anodic oxidation electrical-potential-difference impression approach, an electrical-potential-difference value, and time amount -- they are process terms and conditions, such as subsequent pore wide processing conditions, further -- extent control can be carried out. Moreover, depth  $d$  (die length) of pore 3 can be controlled by thickness of anodic oxidation time amount and aluminum etc., for example, while being 10nm - 100 micrometers, it is.

[0079] Moreover, according to the manufacture approach of this invention, as shown not only in a gestalt but in drawing 6 (c) which was shown in drawing 2 (b) and at which pore has stopped on the way like, it can also consider as the structure which has the pore which penetrates a workpiece.

[0080] The nano structure can also be made by using the further above-mentioned nano structure as mold or a mask. By embedding functional materials, such as a metal and a semi-conductor, into pore as an example of formation of such the nano structure, using as mold the nano structure which has pore Although forming quantum wire or forming a quantum dot by vapor-depositing functional materials, such as a metal and a semi-conductor, using the nano structure which has penetration pore as a mask for vacuum evaporation is mentioned, it will not be limited especially if there is no un-arranging in formation of the nano structure.

[0081] Here, (c) of drawing 7 shows the example in which quantum wire was formed, by embedding a filler 6 into pore 3.

[0082]

[Example] An example is raised to below and this invention is explained.

[0083] As shown in preparation drawing 1 (a) of an example 1 (a) workpiece, what performed mirror plane processing for the front face of aluminum plate of 99.99% of purity by electric-field polish in the mixed solution of perchloric acid and ethanol as a workpiece was prepared.

[0084] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 1 (b), the pore formation start point 2 was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here.

[0085] First, the location which forms a pore formation start point was defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, using the focused ion beam of 30nm of ion beam \*\*\*\*, and ion current abbreviation 3pA, as shown in drawing 4 (a), the pore formation start point was formed by irradiating a focused ion beam in the shape of a dot at a workpiece, as it becomes the repeat of the pattern of a honeycomb mostly at intervals of about 100nm. At this time, the residence time of the focused ion beam in

each dot location was about 10 msec(s).

[0086] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 40 -- it was referred to as V.

[0087] next, a workpiece -- after anodizing -- 5wt(s)% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0088] Evaluation (structure observation)

When the workpiece was observed in FE-SEM (field emission scanning electron microscope), a pore diameter is about 50nm, pore spacing is about 100nm, and, as for each pore, it was checked that the repeat of a honeycomb-like pattern is formed mostly and the high nano structure of the regularity of pore is formed.

[0089] As shown in preparation drawing 3 (b) of an example 2 (a) workpiece, what formed aluminum film with a thickness of about 200nm with resistance heating vacuum deposition was prepared on the quartz substrate as a workpiece.

[0090] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 1 (b), the pore formation start point was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here. The location which forms a pore formation start point was first defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, using the focused ion beam of 30nm of ion beam \*\*\*\*, and ion current abbreviation 3pA, as shown in drawing 4 (b), the pore formation start point was formed by irradiating a focused ion beam in the shape of a dot at a workpiece, as it becomes the repeat of the pattern of forward four square shapes mostly at intervals of about 60nm. At this time, the residence time of the focused ion beam in each dot location was about 100 msec(s).

[0091] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M sulfuric-acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 25 -- it was referred to as V.

[0092] next, a workpiece -- after anodizing -- 5wt(s)% -- the path of pore was extended by dipping between 20min into a phosphoric-acid solution.

[0093] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pore diameter is about 40nm, pore spacing is about 60nm, and it was checked that each pore is mostly formed by the repeat of a forward 4 square-shape-like pattern, and the high nano structure of the regularity of pore is formed.

[0094] The same workpiece as the preparation example 1 of an example 3 (a) workpiece was prepared.

[0095] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 1 (b), the pore formation start point was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here. The location which forms a pore formation start point was first defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, the pore

formation start point was formed in the intersection of each Rhine by irradiating a focused ion beam at the shape of Rhine so that it may become the repeat of Rhine almost parallel to a direction which is different 60 degrees to previous Rhine after irradiating a focused ion beam at the shape of Rhine so that it may become the repeat of Rhine almost parallel at intervals of about 100nm, as shown in drawing 4 (c) using the focused ion beam of 30nm of ion beam \*\*\*\*, and ion current abbreviation 3pA at intervals of about 100nm. A scanning speed and the count of a scan were adjusted so that the sum total of the residence time of the focused ion beam in the intersection of Rhine might be set to about 10 msec(s) at this time.

[0096] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 50 -- it was referred to as V.

[0097] next, a workpiece -- after anodizing -- 5wt(s)% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0098] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 115nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed.

[0099] As shown in preparation drawing 8 (a) of an example 4 (a) workpiece, after forming Ti film used as about 50nm pore trailer material 15 by the spatter and forming a base 13 on the Si substrate 16 What formed about 500nm aluminum film 12 with resistance heating vacuum deposition, and formed about 20nm Pt film which is the conductive film 17 in a spatter about SiO<sub>2</sub> about 20nm film which is the insulator film 18 as a membrane surface 14 further by the spatter was prepared as a workpiece 1.

[0100] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 8 (b), the pore formation start point was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here. The location which forms a pore formation start point was first defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, using the focused ion beam of 50nm of ion beam \*\*\*\*, and ion current abbreviation 60pA, as shown in drawing 11 (a), the pore formation start point was formed by irradiating a focused ion beam in the shape of a dot at a workpiece, as it becomes the repeat of the pattern of a honeycomb mostly at intervals of about 150nm. At this time, the residence time of the focused ion beam in each dot location was about 30 msec(s).

[0101] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed. the acid electrolytic solution -- a 0.3M phosphate water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 70 -- it was referred to as V. It was able to check that anodic oxidation had reached to the pore \*\*\*\* member by reduction in a current value here at the time of anodic oxidation.

[0102] next, a workpiece -- after anodizing -- 5wt(s)% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution (.) (refer to drawing 8 (c))

[0103] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, the pole diameter in a membrane surface is

[ about 70nm and pore spacing of the pole diameter in about 50nm and the alumina film ] about 150nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed. Moreover, when electric measurement of a workpiece was performed, it was checked that surface Pt film is insulated by holding conductivity and coincidence between surface Pt film and Ti film which is a pore terminal point member.

[0104] Example 5 this example is an example which produced the nano structure which has penetration pore by removing parts other than the part which has pore.

[0105] (a) Using the same approach as (a) and (b) of preparation of a workpiece, and the formation process example 1 of (b) pore formation start point, after preparing a workpiece, the pore formation start point was formed in the workpiece.

[0106] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 40 -- it was referred to as V.

[0107] (d) The removal process of parts other than the part which has the removal process pore of parts other than the part which has pore is shown in drawing 6 (a) - (c). The part of the bulk 11 of aluminum of a workpiece was removed by dipping the nano structure as first shown in drawing 6 (a) in the HgCl<sub>2</sub> saturated solution ( drawing 6 (b)). next, a workpiece -- 5wt(s)% -- while removing the barrier layer 4 by dipping between 30min into a phosphoric-acid solution, by extending the path of pore, the nano structure which has the penetration pore 5 was produced ( drawing 6 (c)).

[0108] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 100nm, and it was checked that each penetration pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of penetration pore is formed.

[0109] Example 6 this example is an example which was filled up with the metal in pore and produced the nano structure (quantum wire), using as mold the nano structure which has the pore formed by anodic oxidation.

[0110] (a) As shown in preparation drawing 7 (a) of a workpiece, after forming Ti film used as pore trailer material 15 with a thickness of about 50nm by the spatter and forming a base 13 on the Si substrate 16, what formed the aluminum film 12 with a thickness of about 500nm with resistance heating vacuum deposition further was prepared as a workpiece 1.

[0111] (b) The pore formation start point was formed in the workpiece using the same approach as (b) of an example 1 except the residence time of the focused ion beam in formation process each dot location of a pore formation start point being about 100 msec(s).

[0112] (c) The path of pore was extended after forming pore in a workpiece using the same approach as (c) of the formation process example 1 of pore ( drawing 7 (b)). It was able to check that anodic oxidation had reached to pore trailer material by reduction in a current value here at the time of anodic oxidation.

[0113] (d) When the metal packer into pore performed nickel metal electrodeposition more next, it was filled up with the filler 6 in pore ( drawing 7 (c)). nickel was deposited in the nano hole by nickel restoration dipping and electrodepositing it with the counterelectrode of nickel, in the electrolytic solution which consists of H<sub>3</sub>BO<sub>3</sub> of NiSO<sub>4</sub> and 0.5M of 0.14M.

[0114] Evaluation (structure observation)

When the workpiece before nickel restoration was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 100nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed. Moreover, it was checked that pore has reached to pore trailer material, and the die length of pore was controlled by arranging pore trailer material.

[0115] When the workpiece after nickel \*\*\*\* was furthermore observed in FE-SEM, pore is filled up with nickel and the quantum wire which consists of nickel of about 50nm of sizes was formed.

[0116] The example 1 of the one example comparison of a comparison produced the nano structure by the same approach as an example 1 except having not performed the formation process of (b) pore formation start point in the example 1.

[0117] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, the pore diameter was 30-50nm, pore spacing was 90-100nm, each pore was formed at random and the regularity of pore was low.

[0118] As shown in preparation drawing 1 (a) of an example 7 (a) workpiece, what performed mirror plane processing for the front face of aluminum plate of 99.99% of purity as a workpiece by electrolytic polishing in the inside of the mixed solution of perchloric acid and ethanol was prepared.

[0119] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 1 (b), the pore formation start point was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here.

[0120] The location which forms a pore formation start point was first defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, using the electron beam with a beam diameter of about 10nm, as shown in drawing 4 (a), the pore formation start point was formed by irradiating an electron beam in the shape of a dot at a workpiece, as it becomes the repeat of the pattern of a honeycomb mostly at intervals of about 100nm (2Rv).

[0121] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 40 -- it was referred to as V.

[0122] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0123] Evaluation (structure observation)

When the workpiece was observed in FE-SEM (field emission scanning electron microscope), a pore diameter is about 50nm, pore spacing is about 100nm, and, as for each pore, it was checked that the repeat of a honeycomb-like pattern is formed mostly and the high nano structure of the regularity of pore is formed.

[0124] As shown in preparation drawing 3 (b) of an example 8 (a) workpiece, what formed the aluminum film 12 with a thickness of about 200nm with resistance heating vacuum deposition was prepared on the quartz substrate 13 as a workpiece.

[0125] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in



drawing 1 (b), the pore formation start point was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here. The location which forms a pore formation start point was first defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, using the electron beam with a beam diameter of about 10nm, as shown in drawing 4 (b), the pore formation start point was formed by irradiating an electron beam in the shape of a dot at a workpiece, as it becomes the repeat of the pattern of forward four square shapes mostly at intervals of about 60nm (2Rv).

[0126] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M sulfuric-acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 25 -- it was referred to as V.

[0127] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 20min into a phosphoric-acid solution.

[0128] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pore diameter is about 40nm, pore spacing is about 60nm, and it was checked that each pore is mostly formed by the repeat of a forward 4 square-shape-like pattern, and the high nano structure of the regularity of pore is formed.

[0129] The same workpiece as the preparation example 7 of an example 9 (a) workpiece was prepared.

[0130] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 1 (b), the pore formation start point was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here. The location which forms a pore formation start point was first defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, the pore formation start point was formed in the intersection of each Rhine by irradiating an electron beam at the shape of Rhine so that it may become the repeat of Rhine almost parallel to a direction which is different 60 degrees to previous Rhine after irradiating an electron beam at the shape of Rhine so that it may become the repeat of Rhine almost parallel at intervals of about 100nm, as shown in drawing 4 (c) using an electron beam with a beam diameter of about 30nm at intervals of about 100nm.

[0131] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 50 -- it was referred to as V.

[0132] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0133] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 115nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed.

[0134] As shown in a detail at (a) of preparation drawing 8 of an example 10 (a) workpiece After forming Ti film used as a pore terminal point member 15 with a thickness of about 50nm by the sputter and forming a base 13 on the Si substrate 16 SiO<sub>2</sub> with a thickness of about 20nm which the aluminum film 12 with a thickness of about 500nm is formed with resistance heating vacuum

deposition, and is the insulator film 18 as a membrane surface 14 further What formed Pt film with a thickness of about 20nm which is the conductive film 17 in a spatter about the film by the spatter was prepared as a workpiece 1.

[0135] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 8 (b), the pore formation start point 2 was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here. The location which forms a pore formation start point was first defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, using the electron beam of 10nm of ion beam \*\*\*\*, as shown in drawing 11 (a), the pore formation start point was formed by irradiating an electron beam in the shape of a dot at a workpiece, as it becomes the repeat of the pattern of a honeycomb mostly at intervals of about 150nm.

[0136] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed. the acid electrolytic solution -- a 0.3M phosphate water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 70 -- it was referred to as V. It was able to check that anodic oxidation had reached to the pore terminal point member by reduction in a current value here at the time of anodic oxidation.

[0137] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution (.) (refer to drawing 8 (c))

[0138] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, the pole diameter in a membrane surface is [ about 70nm and pore spacing of the pole diameter in about 50nm and the alumina film ] about 150nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed. Moreover, when electric measurement of a workpiece was performed, it was checked that surface Pt film is insulated by holding conductivity and coincidence between surface Pt film and Ti film which is a pore terminal point member.

[0139] Example 11 this example is an example which manufactured the structure which has the penetrated pore. (a) The same approach as (a) and (b) of an example 7 was used for preparation of a workpiece, and the formation process of (b) pore formation start point.

[0140] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 40 -- it was referred to as V.

[0141] (d) The removal process of parts other than the part which has the removal process pore of parts other than the part which has pore is shown in (a) - (c) of drawing 6 . The part of the bulk 11 of aluminum of a workpiece was removed by dipping the nano structure as first shown in (a) of drawing 6 in the HgCl<sub>2</sub> saturated solution ((b) of drawing 6 ). next, a workpiece -- 5wt(s)% -- while removing the barrier layer 4 by dipping between 30min into a phosphoric-acid solution, by extending the path of pore, the nano structure which has the penetration pore 5 was manufactured ((c) of drawing 6 ).

[0142] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 100nm, and it was checked that each penetration pore is mostly formed by the repeat of a

honeycomb-like pattern, and the high nano structure of the regularity of penetration pore is formed.

[0143] Example 12 this example is an example which was filled up with the metal in pore as mold formed by anodic oxidation, and manufactured the nano structure (quantum wire).

[0144] (a) As shown in a detail at (a) of preparation drawing 7 of a workpiece, after forming Ti film used as a pore terminal point member 15 with a thickness of about 50nm by the sputter and forming a base 13 on the Si substrate 16, what formed the aluminum film 12 with a thickness of about 500nm with resistance heating vacuum deposition further was prepared as a workpiece 1.

[0145] (b) The pore formation start point was formed in the workpiece using the same approach as (b) of the formation process example 7 of a pore formation start point.

[0146] (c) The path of pore was extended after forming pore in a workpiece using the same approach as (c) of the formation process example 7 of pore ((b) of drawing 7 ). It was able to check that anodic oxidation had reached to the pore terminal point member by reduction in a current value here at the time of anodic oxidation.

[0147] (d) When the metal packer into pore next performed nickel metal electrodeposition, it was filled up with the filler 6 in pore ((c) of drawing 7 ). nickel was deposited in the nano hole by nickel restoration dipping and electrodepositing it with the counterelectrode of nickel, in the electrolytic solution which consists of H<sub>3</sub>BO<sub>3</sub> of NiSO<sub>4</sub> and 0.5M of 0.14M.

[0148] Evaluation (structure observation)

When the workpiece before nickel restoration was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 100nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed. Moreover, it was checked that pore has reached to a pore terminal point member, and the die length of pore was controlled by arranging a pore terminal point member.

[0149] When the workpiece after nickel restoration was furthermore observed in FE-SEM, pore is filled up with nickel and the quantum wire which consists of nickel of about 50nm of sizes was formed.

[0150] As shown in example 13(a) workpiece preparation drawing 9 (a), what performed mirror plane processing for the front face of aluminum plate of 99.99% of purity by electric-field polish in the mixed solution of perchloric acid and ethanol as a workpiece was prepared.

[0151] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 9 (b), the pore formation start point was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here.

[0152] The location which forms a pore formation start point was first defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, pyrene gas was introduced in focusing ion beam machining equipment as gas for membrane surface formation. Furthermore, the pore formation start point was formed using the focused ion beam of 30nm of ion beam \*\*\*\*, and ion current abbreviation 3pA by irradiating a focused ion beam so that the non-irradiating location of a focused ion beam may become the repeat of the pattern of a honeycomb mostly at intervals of about 150nm, as shown in drawing 10 (a). The membrane surface containing C is formed in the exposure location of a focused ion beam at this time.

[0153] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M phosphate water solution -- using -- a constant

temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 70 -- it was referred to as V.

[0154] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0155] Evaluation (structure observation)

When the workpiece was observed in FE-SEM (field emission scanning electron microscope), a pore diameter is about 50nm, pore spacing is about 150nm, and, as for each pore, it was checked that the repeat of a honeycomb-like pattern is formed mostly and the high nano structure of the regularity of pore is formed.

[0156] As shown in example 14(a) workpiece preparation drawing 3 (b), what formed about 200nm aluminum film 12 with resistance heating vacuum deposition was prepared on the quartz substrate 13 as a workpiece.

[0157] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 9 (b), the pore formation start point was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here.

[0158] First, the location which forms a pore formation start point was defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, pyrene gas was introduced in focusing ion beam machining equipment as gas for membrane surface formation. Furthermore, the pore formation start point was formed using the focused ion beam of 30nm of ion beam \*\*\*\*, and ion current abbreviation 3pA by irradiating a focused ion beam so that the non-irradiating location of a focused ion beam may become the repeat of the pattern of forward four square shapes mostly at intervals of about 150nm, as shown in drawing 10 (b). The membrane surface containing C is formed in the exposure location of a focused ion beam at this time.

[0159] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 60 -- it was referred to as V.

[0160] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0161] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 150nm, and it was checked that each pore is formed by the repeat of a \*\*\*\* right 4 square-shape-like pattern, and the high nano structure of the regularity of pore is formed.

[0162] The same workpiece as the example 15(a) workpiece preparation example 13 was prepared.

[0163] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 9 (b), the pore formation start point was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here.

[0164] First, the location which forms a pore formation start point was defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, W(CO) 6 gas was introduced in focusing ion beam machining equipment as gas for membrane surface formation. Next, the focused ion beam of 30nm of ion beam \*\*\*\* and ion

current abbreviation 3pA is used. After irradiating a focused ion beam in the shape of Rhine so that it may become the repeat of almost parallel Rhine at intervals of about 150nm as shown in drawing 10 (c) The pore formation start point was formed in the field surrounded by each Rhine by irradiating a focused ion beam in the shape of Rhine so that it may become the repeat of Rhine almost parallel to a direction which is different 60 degrees to previous Rhine at intervals of about 150nm. The membrane surface containing W is formed in the exposure location of a focused ion beam at this time.

[0165] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M phosphate water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 80 -- it was referred to as V.

[0166] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0167] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 170nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed.

[0168] Example 16 this example is an example which manufactured the nano structure which has penetration pore by removing parts other than the part which has pore.

[0169] (a) Using the same approach as (a) and (b) of the formation process example 13 of workpiece preparation and (b) pore formation start point, after preparing a workpiece, the pore formation start point was formed in the workpiece.

[0170] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 70 -- it was referred to as V.

[0171] (d) The removal process of parts other than the part which has the removal process pore of parts other than the part which has pore is shown in (a) - (c) of drawing 6 . The membrane surface 14 was removed by carrying out Ar ion etching of the workpiece as first shown in drawing 9 (c) ((a) of drawing 6 ). Next, the part of the bulk 11 of aluminum of a workpiece was removed by dipping a workpiece in the HgCl<sub>2</sub> saturated solution ((b) of drawing 6 ). next, a workpiece -- 5wt(s)% -- while removing the barrier layer 4 by dipping between 30min into a phosphoric-acid solution, by extending the path of pore, the nano structure which has the penetration pore 5 was manufactured ((c) of drawing 6 ).

[0172] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 150nm, and it was checked that each penetration pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of penetration pore is formed.

[0173] Example 17 this example is an example which was filled up with the metal in pore and manufactured the nano structure (quantum wire), using as mold the nano structure which has the pore formed by anodic oxidation.

[0174] (a) As shown in a detail at (a) of workpiece preparation drawing 7 , after forming Ti film used as pore trailer material 15 with a thickness of about 50nm by the spatter and forming a base

13 on the Si substrate 16, what formed the aluminum film 12 with a thickness of about 500nm with resistance heating vacuum deposition further was prepared as a workpiece 1.

[0175] (b) The pore formation start point was formed in the workpiece using the same approach as (b) of the formation process example 13 of a pore formation start point.

[0176] (c) The path of pore was extended after forming pore in a workpiece using the same approach as (c) of the formation process example 13 of pore ((b) of drawing 7 ). It was able to check that anodic oxidation had reached to pore trailer material by reduction in a current value here at the time of anodic oxidation.

[0177] (d) When the metal packer into pore performed nickel metal electrodeposition more next, it was filled up with the filler 6 in pore ((c) of drawing 7 ). nickel was deposited in the nano hole by nickel restoration dipping and electrodepositing it with the counterelectrode of nickel, in the electrolytic solution which consists of 0.14M NiSO<sub>4</sub> and 0.5MH<sub>3</sub>BO<sub>3</sub>.

[0178] Evaluation (structure observation)

When the workpiece before nickel restoration was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 150nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed. Moreover, it was checked that pore has reached to pore trailer material, and the die length of pore was controlled by arranging pore trailer material.

[0179] When the workpiece after nickel restoration was furthermore observed in FE-SEM, pore is filled up with nickel and the quantum wire which consists of nickel of about 50nm of sizes was formed.

[0180] As shown in example 18(a) workpiece preparation drawing 9 (a), what performed mirror plane processing for the front face of aluminum plate of 99.99% of purity by electric-field polish in the mixed solution of perchloric acid and ethanol as a workpiece was prepared.

[0181] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 9 (b), the pore formation start point was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here.

[0182] First, the location which forms a pore formation start point was defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, pyrene gas was introduced in electron beam irradiation equipment as gas for membrane surface formation. Furthermore, the pore formation start point was formed using the electron beam with a beam diameter of about 10nm by irradiating an electron beam so that the non-irradiating location of an electron beam may become the repeat of the pattern of a honeycomb mostly at intervals of about 150nm, as shown in drawing 10 (a). The membrane surface containing C is formed in the exposure location of an electron beam at this time.

[0183] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M phosphate water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 70 -- it was referred to as V.

[0184] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0185] Evaluation (structure observation)

When the workpiece was observed in FE-SEM (field emission scanning electron microscope), a pole diameter is about 50nm, pore spacing is about 150nm, and, as for each pore, it was checked

that the repeat of a honeycomb-like pattern is formed mostly and the high nano structure of the regularity of pore is formed.

[0186] As shown in example 19(a) workpiece preparation drawing 9 (a), what formed aluminum film with a thickness of about 200nm with resistance heating vacuum deposition was prepared on the quartz substrate as a workpiece.

[0187] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 9 (b), the pore formation start point was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here.

[0188] First, the location which forms a pore formation start point was defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, pyrene gas was introduced in electron beam irradiation equipment as gas for membrane surface formation. Furthermore, the pore formation start point was formed using the electron beam with a beam diameter of about 10nm by irradiating an electron beam so that the non-irradiating location of an electron beam may become the repeat of the pattern of forward four square shapes mostly at intervals of about 150nm, as shown in drawing 10 (b). The membrane surface containing C is formed in the exposure location of an electron beam at this time.

[0189] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 60 -- it was referred to as V.

[0190] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0191] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 150nm, and it was checked that each pore is mostly formed by the repeat of a forward 4 square-shape-like pattern, and the high nano structure of the regularity of pore is formed.

[0192] The same workpiece as the example 20(a) workpiece preparation example 18 was prepared.

[0193] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 9 (b), the pore formation start point was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here.

[0194] First, the location which forms a pore formation start point was defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, W(CO) 6 gas was introduced in electron beam irradiation equipment as gas for membrane surface formation. Next, the pore formation start point was formed in the field surrounded by each Rhine by irradiating an electron beam at the shape of Rhine so that it may become the repeat of Rhine almost parallel to a direction which is different 60 degrees to previous Rhine after irradiating an electron beam at the shape of Rhine so that it may become the repeat of Rhine almost parallel at intervals of about 150nm, as shown in drawing 10 (c) using an electron beam with a beam diameter of about 10nm at intervals of about 150nm. The membrane surface containing W is formed in the exposure location of an electron beam at this time.

[0195] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c).

the acid electrolytic solution -- a 0.3M phosphate water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 80 -- it was referred to as V.

[0196] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0197] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 170nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed.

[0198] Example 21 this example is an example which manufactured the nano structure which has penetration pore by removing parts other than the part which has pore.

[0199] (a) Using the same approach as (a) and (b) of the formation process example 18 of workpiece preparation and (b) pore formation start point, after preparing a workpiece, the pore formation start point was formed in the workpiece.

[0200] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 70 -- it was referred to as V.

[0201] (d) The removal process of parts other than the part which has the removal process pore of parts other than the part which has pore is shown in (a) - (c) of drawing 6. The membrane surface 14 was removed by carrying out Ar ion etching of the workpiece as first shown in (c) of drawing 9 ((a) of drawing 6). Next, the part of the bulk 11 of aluminum of a workpiece was removed by dipping a workpiece in the HgCl<sub>2</sub> saturated solution ((b) of drawing 6). next, a workpiece -- 5wt(s)% -- while removing the barrier layer 4 by dipping between 30min into a phosphoric-acid solution, by extending the path of pore, the nano structure which has the penetration pore 5 was manufactured ((c) of drawing 6).

[0202] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 150nm, and it was checked that each penetration pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of penetration pore is formed.

[0203] Example 22 this example is an example which was filled up with the metal in pore and manufactured the nano structure (quantum wire), using as mold the nano structure which has the pore formed by anodic oxidation.

[0204] (a) As shown in a detail at (a) of workpiece preparation drawing 7, after forming Ti film used as pore trailer material 15 with a thickness of about 50nm by the spatter and forming a base 13 on the Si substrate 16, what formed the aluminum film 12 with a thickness of about 500nm with resistance heating vacuum deposition further was prepared as a workpiece 1.

[0205] (b) The pore formation start point was formed in the workpiece using the same approach as (b) of the formation process example 18 of a pore formation start point.

[0206] (c) The path of pore was extended after forming pore in a workpiece using the same approach as (c) of the formation process example 18 of pore ((b) of drawing 7). It was able to check that anodic oxidation had reached to pore trailer material by reduction in a current value here at the time of anodic oxidation.

[0207] (d) When the metal packer into pore performed nickel metal electrodeposition more next,



it was filled up with the filler 6 in pore ((c) of drawing 7). nickel restoration -- 0.14M NiSO<sub>4</sub> and 0.5MHBO<sub>3</sub> from -- nickel was deposited in the nano hole by being dipped and electrodeposited with the counterelectrode of nickel in the becoming electrolytic solution.

[0208] Evaluation (structure observation)

When the workpiece before nickel restoration was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 150nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed. Moreover, it was checked that pore has reached to pore trailer material, and the die length of pore was controlled by arranging pore trailer material.

[0209] When the workpiece after nickel restoration was furthermore observed in FE-SEM, pore is filled up with nickel and the quantum wire which consists of nickel of about 50nm of sizes was formed.

[0210]

[Effect of the Invention] As explained above, there is the following effectiveness in this invention.

(1) Control of the array of pore, spacing, a location, a direction, etc. is possible, and it becomes possible to produce the nano structure (anodic oxidation alumina) which has the pore by which the pore excellent in linearity has been arranged regularly, and pore.

(2) the workpiece which has irregularity in a front face since particle radiation is used for formation of a pore formation start point -- also receiving -- a pore formation start point -- homogeneity -- it can form highly.

[0211] (3) Since it is not necessary to put a pressure on a workpiece when forming a pore formation start point, since particle radiation is used for formation of a pore formation start point, a mechanical strength can apply also to the workpiece which is not strong.

(4) Even when the film is formed in a workpiece front face, it is possible to remove said film partially and to form a pore formation start point in said film by irradiating a corpuscular ray.

[0212] (5) Since corpuscular ray irradiation equipment is used, it is easy to position a pattern with high precision using an attached secondary electron image observation function etc.

(6) Since corpuscular ray irradiation equipment is used, a pore formation start point can be formed by straight-writing. Therefore, the process resist spreading required for stamper manufacture etc., electron beam exposure, and time-consuming [ like resist removal ] is unnecessary, and it is possible to form a pore formation start point for a short time.

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## TECHNICAL FIELD

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[Field of the Invention] This invention relates to the manufacture approach of the nano structure and the nano structure which have available pore in the large range especially as functional materials, such as an electron device, and an optical device, a micro device, a structural material, etc. about the structure which has the pore and this pore which were manufactured by the manufacture approach of pore, and the list by this manufacture approach.

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## PRIOR ART

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[Description of the Prior Art] In a metal and the thin film of a semi-conductor, a thin line, and a dot, there is a unique thing for which electric, optical, and chemical property are shown by shutting up a motion of an electron in size smaller than a certain characteristic die length. The

interest about the ingredient (nano structure) which has structure more detailed than several 100nm as high-performance material from such a viewpoint is increasing.

[0003] As the manufacture approach of such the nano structure, photolithography is begun and the method of manufacturing the nano structure directly with semi-conductor processing techniques including detailed pattern formation techniques, such as electron beam lithography and X-ray lithography, is mentioned, for example.

[0004] Moreover, the attempt which is going to realize the new nano structure is in the base in the regular structure formed automatically, i.e., the structure formed in a self-regulation target, besides such a manufacture approach. Since such technique may be able to manufacture the detailed and special structure which turns around the conventional approach a top depending on the fine structure used as the base, many researches are beginning to be done.

[0005] The anodic oxidation which can manufacture easily the nano structure which has the pore of nano size with sufficient control as such self-regular technique is mentioned. For example, the anodic oxidation alumina which manufactures aluminum and its alloy by anodizing in an acidic bath is known.

[0006] If aluminum plate is anodized in an acid electrolyte, a porosity oxide film will be formed (for example, reference, such as R.C.Furneaux, W.R.Rigby&A.P.Davids, "NATURE", Vol.337, and P147 (1989)). The very detailed cylindrical pore (nano hole) whose diameter is several nm - hundreds of nm has the description of this porosity oxide film in having the specific geometric structure of arranging in parallel at intervals of several nm - hundreds of nm (cell size). The pore of the shape of this cylinder has a high aspect ratio, and is excellent also in the uniformity of the path of a cross section. Moreover, when the path and spacing of this pore adjust the current in the case of anodic oxidation, and an electrical potential difference, the thickness of an oxide film and the depth of pore are controlling the time amount of anodic oxidation, and a certain amount of control is possible for them.

[0007] Moreover, the method of performing two steps of anodic oxidation, in order to improve the perpendicularity, the linearity, and the independence of pore, Namely, once removing the porosity oxide film anodized and formed, it anodizes again. The method of manufacturing the pore which shows better perpendicularity, linearity, and an independence is proposed ("Jpn.Journal of Applied Phisics" , Vol.35, Part2, No.1B, pp.L126-L129, 1 January15, 996 issue). Here, this approach uses that the hollow of the front face of the aluminum plate made when removing the anodic oxide film formed by the first anodic oxidation serves as a pore formation start point of the 2nd anodic oxidation.

[0008] Furthermore, it anodizes, after forming the hollow which forces the approach of using a stamper and forming a pore formation start point in order to improve the controllability of the configuration of pore, spacing, and a pattern, i.e., the substrate which equipped the front face with two or more projections, on the surface of an aluminum plate, and can do it as a pore formation start point, and the method of manufacturing the pore which shows the controllability of a better configuration, spacing, and a pattern is also proposed (JP,10-121292,A).

[0009] Various application which paid its attention to the specific geometrical structure of this anodic oxidation alumina is tried. Although the description by Masuda is detailed, an application is listed hereafter. For example, there are application as a coat using the abrasion resistance of an oxide film on anode and insulation-proof and application of fill TAHE which exfoliates a coat. Furthermore, various application including coloring, a magnetic-recording medium, EL light emitting device, an electrochromic element, an optical element, a solar battery, and a gas sensor is tried from using the technique filled up with a metal, a semi-conductor, etc. in a nano hole, and

the replica technique of a nano hole. Furthermore, the application to the directions of many, such as the quantum effectiveness devices, such as quantum wire and an MIM component, and a molecule sensor using a nano hole as a chemical reaction place, is expected (Masuda "solid-state physics", 31,493 (1996)).

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## EFFECT OF THE INVENTION

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[Effect of the Invention] As explained above, there is the following effectiveness in this invention.

(1) Control of the array of pore, spacing, a location, a direction, etc. is possible, and it becomes possible to produce the nano structure (anodic oxidation alumina) which has the pore by which the pore excellent in linearity has been arranged regularly, and pore.

(2) the workpiece which has irregularity in a front face since particle radiation is used for formation of a pore formation start point -- also receiving -- a pore formation start point -- homogeneity -- it can form highly.

[0211] (3) Since it is not necessary to put a pressure on a workpiece when forming a pore formation start point, since particle radiation is used for formation of a pore formation start point, a mechanical strength can apply also to the workpiece which is not strong.

(4) Even when the film is formed in a workpiece front face, it is possible to remove said film partially and to form a pore formation start point in said film by irradiating a corpuscular ray.

[0212] (5) Since corpuscular ray irradiation equipment is used, it is easy to position a pattern with high precision using an attached secondary electron image observation function etc.

(6) Since corpuscular ray irradiation equipment is used, a pore formation start point can be formed by straight-writing. Therefore, the process resist spreading required for stamper manufacture etc., electron beam exposure, and time-consuming [ like resist removal ] is unnecessary, and it is possible to form a pore formation start point for a short time.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] The manufacture approach of the direct nano structure by the semi-conductor processing technique expressed previously and pore has problems, like the badness of the yield and the cost of equipment are high, and technique which can be manufactured with sufficient repeatability by simple technique is desired.

[0011] Since the technique of anodic oxidation from such a viewpoint can manufacture the nano structure and pore with sufficient control comparatively easily, it is desirable.

[0012] However, although many techniques in which the pore object manufactured only by the usual anodic oxidation controlled the configuration of the pore and a pattern were developed, there was a limitation in the control. As control in anodic oxidation, the thing controllable to some extent is known [ depth / of pore / pole diameter ] for time amount in pore spacing on the anodic oxidation electrical potential difference at pore wide processing. Furthermore, the example which manufactured the regulation-ized nano hole arranged in the shape of a honeycomb by anodizing under suitable anodic oxidation conditions by Masuda and others as an example which controlled the array of pore is reported. However, in this regulation-ized nano hole, there were technical problems, like there is a limit to be anodized [ of long duration ] in spacing of the pore which can be manufactured.

[0013] Moreover, in the approach of performing two steps of anodic oxidation, although the

perpendicularity, the rectilinear-propagation nature, and the independence of pore have improved and the good parts of spacing of pore and the controllability of a pattern also existed still more nearly locally, when seen on the whole, spacing and the pattern of pore had the technical problem that these controllabilities were not good rather than were fixed.

[0014] In the approach of furthermore forming a pore formation start point using a stamper, the controllability of the configuration of pore, spacing, and a pattern had the technical problem which is described below, although improved.

(1) Since the stamper is used, it is difficult to form a pore formation start point in a front face to an irregular workpiece at homogeneity.

(2) Since there is risk of a workpiece being destroyed to the workpiece whose mechanical strength is not strong since it is necessary to put a pressure on a workpiece at the time of stamper use, application is difficult.

[0015] (3) Since it is difficult to expose aluminum on a front face to a workpiece by which the film was formed in the aluminum front face since compression by the stamper is used, it is difficult to make a stamp location into a pore formation start point.

(4) It is not easy to have to use a hydraulic press at the time of use of a stamper, and to position a pattern with high precision.

(5) It is not easy for manufacture of a stamper to manufacture without a defect the stamper which must use ultra-fine processing technology time-consuming [ like electron beam lithography ], and has the projection of uniform high density for a short time.

[0016] The purpose of this invention is to solve these technical problems. That is, the purpose of this invention is offering the technique which controls the configuration of pore, spacing, a pattern, a location, a direction, etc. in the structure which has the pore and pore which are manufactured by anodic oxidation.

[0017] It is providing coincidence with the technique which can be manufactured in a short time easily possible [ highly precise control of a pattern location ], without receiving constraint of existence of the film of the gestalt of a workpiece, for example, surface irregularity, a mechanical strength, and a front face etc. in this invention.

[0018] It is using as the base the nano structure which has the pore furthermore manufactured with the application of this technique, indicating the new nano structure and a nano structure device, and making use possible for a nano hole in directions various as a functional material.

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## MEANS

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[Means for Solving the Problem] Then, the manufacture approach of the pore of this invention is characterized by having the process which irradiates a corpuscular ray at a workpiece, and the process which forms pore more at said workpiece for anodizing the workpiece which irradiated said corpuscular ray.

[0020] This invention is characterized also by said corpuscular ray being a charged particle beam again. Moreover, said corpuscular ray is characterized also by being a focused ion beam or an electron beam.

[0021] This invention is characterized by being the process which removes said film alternatively again by irradiating said corpuscular ray at the film with which the process which irradiates said corpuscular ray controls the anodic oxidation arranged on the front face of said workpiece.

[0022] This invention is characterized by being the process which forms in the front face of said

workpiece alternatively the film which controls anodic oxidation again from the raw material contained in the ambient atmosphere in which the processes which irradiate said corpuscular ray surround said workpiece.

[0023] According to this invention, pore can be formed in the location of said pore formation start point by irradiating a corpuscular ray at a workpiece, and being able to form a pore formation start point in a desired location, consequently anodizing a workpiece. For this reason, according to this invention, control of the array of the pore of the structure of a nano meter scale, spacing, a location, a direction, etc. is possible.

[0024] the workpiece which has irregularity in a front face since the manufacture approach of this invention uses the exposure of a corpuscular ray for formation of a pore formation start point at coincidence -- also receiving -- a pore formation start point -- homogeneity -- forming highly is easy.

[0025] Moreover, since it does not need to put a pressure on a workpiece when forming a pore formation start point, since the manufacture approach of this invention uses the exposure of a corpuscular ray for formation of a pore formation start point, a mechanical strength can apply it also to the workpiece which is not strong.

[0026] Moreover, even when the film is formed in a workpiece front face, the manufacture approach of this invention is irradiating a corpuscular ray at said film, and said film is removed partially and it can form a pore formation start point.

[0027] Moreover, since the manufacture approach of this invention uses corpuscular ray irradiation equipment, it is easy the approach to position a pattern with high precision using an attached secondary electron image observation function etc.

[0028] Furthermore, since the manufacture approach of this invention uses corpuscular ray irradiation equipment, it can form a pore formation start point by straight-writing. Therefore, the process resist spreading required for stamper manufacture etc., electron beam exposure, and time-consuming [ like resist removal ] is unnecessary, and it is possible to form a pore formation start point for a short time.

[0029]

[Embodiment of the Invention] Hereafter, the manufacture approach of the structure which has the pore of this invention and pore is mainly explained using drawing 1 . Drawing 1 is process drawing showing an example of the manufacture approach of the nano structure of this invention. Following process (a) - (c) mainly corresponds to (a) - (c) of drawing 1 .

[0030] (a) Prepare the workpiece 1 which forms preparation \*\*\*\* of a workpiece, and pore. Although the member which uses aluminum as a principal component is mentioned as a what workpiece this invention can be desirable and can apply, if it is the quality of the material in which the pore formation by anodic oxidation is possible, it will not be limited especially. For example, the member which uses Si, InP, or GaAs as a principal component can be used as a workpiece of this invention.

[0031] The example of the gestalt of the workpiece which this invention can be desirable and can apply is shown in (a) - (d) of drawing 3 . The bulk 11 which uses aluminum as shown in drawing 3 (a) as a principal component as an example of the 1st gestalt is mentioned. Moreover, in the bulk 11 which uses aluminum as a principal component, in order to give smooth nature to a front face, even if it is not necessarily required to perform mirror-polishing processing and some surface irregularity exists, this invention is applicable.

[0032] Next, what formed the film 12 which uses aluminum as a principal component on the base 13 as shown in (b) of drawing 3 as an example of the 2nd gestalt is mentioned. At this time,

the thing in which the film of one or more layers was formed on substrates, such as insulator substrates and silicon including quartz glass, and semi-conductor substrates including gallium arsenide, and these substrates is mentioned as a base 13. However, if there is no un-arranging in the pore formation by anodic oxidation of the film 12 which uses aluminum as a principal component, the quality of the material of a base 13, thickness, especially a mechanical strength, etc. will not be limited. For example, if what formed the film of pore formation terminal point members, such as Ti and Nb, on the substrate as a base 13 is used, it will also become possible to raise the homogeneity of the depth of pore. Moreover, as for the membrane formation approach of the film 12 which carries out a principal component, the membrane formation approach of arbitration including resistance heating vacuum evaporation, EB vacuum evaporation, a spatter, and CVD can apply aluminum. Moreover, in the film 12 which uses aluminum as a principal component, even if the surface irregularity resulting from existence of a grain etc. exists, this invention is applicable.

[0033] Next, what formed the membrane surface 14 in the thing ( drawing 3 (c)) which formed the membrane surface 14 in the bulk 11 which uses aluminum as a principal component as an example of the 3rd gestalt, or the thing which formed in base top 13 the film 12 which uses aluminum as a principal component ( drawing 3 (d)) is mentioned. Although an insulator, bulb metals (Nb, Ti, Ta, Zr, Hf, etc.), or C is mentioned, for example, if it is the quality of the material which is not inconvenient to the pore formation by anodic oxidation as the quality of the material of the membrane surface 14 formed in a front face at this time, it will not be limited especially.

[0034] Moreover, although not only the film of a monolayer but the film more than two-layer is mentioned as a membrane surface 14, if there is no un-arranging in the pore formation by anodic oxidation, neither the quality of the material of each layer nor especially its combination will be limited. For example, as shown in drawing 8 (a), in the case of the workpiece which is the two-layer film which is the conductive film 17 which the membrane surface 14 formed the insulator film 18 and on it, the manufactured nano structure becomes like drawing 8 (c), but it also becomes possible to apply the nano structure manufactured by using the conductive film on the top face of the maximum as a microelectronic device. Moreover, in a membrane surface 14, even if the surface irregularity resulting from existence of a grain etc. exists, this invention is applicable.

[0035] Although what has what [ not only / tabular ] is smooth as a configuration of the workpiece of this invention but a curved surface, the thing which has a certain amount of irregularity and level difference on a front face are mentioned, if there is no un-arranging in the pore formation by anodic oxidation, it will not be limited especially.

[0036] (b) It is irradiating a corpuscular ray 10 (their being a focused ion beam and an electron beam as a concrete example) at the formation process above-mentioned workpiece 1 of a pore formation start point, and form the pore formation start point 2 in a desired location.

[0037] A setup of the exposure location of the corpuscular ray to a workpiece can be carried out by being easily highly precise by using the observation means attached to corpuscular ray irradiation equipment.

[0038] The method of detecting the secondary electron generated especially as this observation means when corpuscular rays, such as a focused ion beam and an electron beam, are scanned on a sample, and obtaining a scan image is mentioned. By this approach, a corpuscular ray will be irradiated at a workpiece at the time of observation. However, it is possible for the effect of the particle radiation at the time of setting up the patterning location of a workpiece to be substantially disregarded by obtaining a scan image using the corpuscular ray of an amount small

enough.

[0039] The approach of scanning the corpuscular ray itself and moving an exposure location as an approach of moving the exposure location of a corpuscular ray, the method of moving a workpiece, or the approach of combining the both is mentioned. Although the method of moving the corpuscular ray itself here is rational in equipment, since a movable distance has a limit, it is thought that the approach of combining both is suitable to form a pore formation start point in a large area and high density. Moreover, if the sample stage in which highly precise position control is possible also about the approach of moving a workpiece is used, it is possible to apply this invention.

[0040] Next, the example of the formation approach of the pore formation start point by the particle radiation of this invention is explained using drawing 4 , drawing 10 , and drawing 11 . At this time, drawing 4 (a), drawing 4 (c), drawing 10 (a), drawing 10 (c), and drawing 11 (a) are the examples which formed the pore formation start point in the shape of a honeycomb mostly. Moreover, drawing 4 (b), drawing 4 (d), drawing 10 (b), drawing 10 (d), and drawing 11 (b) are the examples which formed the pore formation start point in the shape of forward 4 square shape mostly. Although various examples can be considered besides the example shown here, if there is no un-arranging in the pore formation by anodic oxidation, it will not be limited especially.

[0041] When it roughly divides, there are the following three approaches among the formation approaches of the pore formation start point by the particle radiation of this invention. a primary method is irradiating a corpuscular ray on a workpiece front face, and is physical in a workpiece front face -- and -- or it is the approach of making it changing chemically.

[0042] And the second approach is the approach of removing a mask partially by irradiating a corpuscular ray on the mask (film which controls anodic oxidation) formed in the workpiece front face, making expose the front face of a workpiece partially, and making that a pore formation start point.

[0043] Furthermore, the third approach is irradiating a corpuscular ray on a workpiece front face, and is the approach of forming in a workpiece front face a mask (film which controls anodic oxidation) around a part making into a pore formation start point from the raw material which exists in the ambient atmosphere which surround a workpiece.

[0044] First, a primary method is explained. There are an approach of irradiating a corpuscular ray alternatively only in a location making into a pore formation start point and the approach of forming a pore formation start point with the difference of the exposure, although a corpuscular ray is irradiated besides a location to make into a pore formation start point at a primary method.

[0045] It is the approach ( drawing 4 (a), (b)) of irradiating a corpuscular ray only in a location making into the above and a pore formation start point as an example of the approach of irradiating a corpuscular ray alternatively at a workpiece at the field of plurality [ shape / of a dot (circle) ], for example. By the approach shown in drawing 4 (a) and (b), after making a corpuscular ray stay at a certain dot location 31, it repeats moving to the dot location 31 of a degree and making a corpuscular ray stay, and it is performed. A pore formation start point can be formed in the field to which the corpuscular ray was irradiated by doing in this way. It is possible by shortening transit time between dots very much compared with the residence time in a dot location to lose substantially the effect of the particle radiation in the case of migration between dots to stop a corpuscular ray here at the time of migration between dots.

[0046] moreover -- as the example of the approach of forming a pore formation start point with the difference of the exposure of the above-mentioned corpuscular ray -- a workpiece -- a corpuscular ray -- the shape of Rhine -- and there is the approach ( drawing 4 (c), (d)) of

irradiating so that an intersection may be formed. This approach is irradiating a corpuscular ray in the shape of Rhine in the different direction at a workpiece, and forms at least the part (intersection) irradiated twice. As shown in drawing 4 (c) and (d), the approach of scanning a corpuscular ray in the shape of [ which intersects perpendicularly mutually ] Rhine 32, and irradiating it only once is more specifically mentioned. In this approach, since the multiple-times exposure of the corpuscular ray is carried out compared with that perimeter on the intersection 33 of Rhine, a pore formation start point can be formed in the intersection 33 of Rhine.

[0047] Here, why the part which irradiated the corpuscular ray, or a part with many corpuscular ray exposures (count) becomes a pore formation start point is explained below. chemical change (presentation change etc.) according to an ion implantation when a focused ion beam is used as a corpuscular ray -- and -- or it is presumed that the condition of differing from a perimeter is formed in a workpiece front face, the singular point at the time of it being anodic oxidation (pore formation start point) comes, and anodic oxidation advances by physical change by ion etching.

[0048] Moreover, as a corpuscular ray, when an electron ray is used, the physical conditions of changing, having reached or differing from a perimeter by chemical change (presentation change etc.), such as thermal deformation by electron beam exposure, damage generating, and evaporation, were formed in the workpiece front face, the singular point at the time of it being anodic oxidation (pore formation start point) came, and it is presumed that anodic oxidation advances.

[0049] The above-mentioned manufacture approach is irradiating a corpuscular ray on the surface of a workpiece, and makes directly the part which produced and cheated out of a certain change a pore formation start point at a workpiece. However, the formation approach of the pore formation start point of this invention is not restricted to the above-mentioned approach.

[0050] Next, the second approach of above mentioned this invention is explained. This approach arranges beforehand the film (membrane surface) 14 which controls anodic oxidation on the surface of a workpiece, as shown in drawing 3 (c), drawing 3 (d), or drawing 8 (a), a corpuscular ray is irradiated, by this, the above-mentioned film is partially removed only in the location of a request of this film, and the front face of a workpiece is exposed in it ( drawing 8 (b), drawing 11 (a), (b)). Let the front face of the exposed workpiece be a pore formation start point by this approach. As an example of the approach of irradiating a corpuscular ray only in a location making into the above and a pore formation start point, the approach ( drawing 11 (a), (b)) of irradiating a corpuscular ray in the shape of a dot (circle) is mentioned to a workpiece, for example. By the approach shown in drawing 11 (a) and (b), after making a corpuscular ray stay at a certain dot location 37, it repeats moving to the dot location 37 of a degree and making a corpuscular ray stay, and it is performed. The field which removed the membrane surface 14 of the field where the corpuscular ray was irradiated, was made to expose processing-ed, and was exposed by doing in this way can be made into a pore formation start point. It is possible by shortening transit time between dots very much compared with the residence time in a dot location to lose substantially the effect of the particle radiation in the case of migration between dots to stop a corpuscular ray here at the time of migration between dots.

[0051] Next, the third approach of above mentioned this invention is explained. Contrary to the second approach of the above, this approach can arrange the film 14 which controls the anodic oxidation described above on the surface of the workpiece only in a desired location by irradiating a corpuscular ray to the field of a request of a workpiece in the ambient atmosphere 7 containing the raw material for forming the film which controls anodic oxidation, as shown in drawing 9 (b). And as a result, the front face (front face of a workpiece in which the film 14 is



not formed) of the workpiece which is not irradiating the corpuscular ray can be made into a pore formation start point ( drawing 10 ). as an example of the formation approach of the pore formation start point by this approach, a pore formation start point can be formed by leaving a pattern ( drawing 10 (a) and (b) -- the shape of a dot (circle), and drawing 10 (c) -- \*\*\*\* -- the shape of a rectangle) making into a pore formation start point, and irradiating the front face 35 of the workpiece which remains with a corpuscular ray (d). Especially, it is drawing 10 (c) (d), In the shown pattern, a corpuscular ray can be scanned in the shape of Rhine on a workpiece front face, and the field 38 surrounded by the film which controls anodic oxidation can be made into a pore formation start point by placing the film which controls Rhine-like anodic oxidation and arranging spacing. Therefore, since a pore formation start point can be formed simply, it is desirable.

[0052] As film which controls the above-mentioned anodic oxidation, although an insulator is mentioned, for example, if it is the ingredient which can control anodic oxidation of a workpiece, a conductor or a semi-conductor will also be available. However, \*\* with desirable removing noble metals, in using a conductor in order to anodize to stability.

[0053] Why the non-irradiating location of the corpuscular ray in the inside of the ambient atmosphere containing the raw material for forming the film which controls anodic oxidation here becomes a pore formation start point is explained. In a particle-radiation location, the film is formed for the above-mentioned raw material on the workpiece of a particle-radiation location of a pyrolysis etc. And since the pore formation to the workpiece which exists directly under the film is controlled with the formed film, it is presumed that formation (growth) of the pore in corpuscular ray a non-irradiating location advances.

[0054] The ingredient which has a metal as a component is mentioned as the 1st mode of the class of raw material for forming the film which controls the above-mentioned anodic oxidation. for example, -- W -- (-- CO --) -- six -- Mo -- (-- CO --) -- six -- like -- a metal carbonyl -- metallurgy -- a group -- an organic compound -- SiCl -- four -- TiCl -- four -- ZrCl -- four -- TaCl -- four -- MoCl -- five -- WF -- six -- etc. -- a metal -- a halogenide -- or -- SiH -- four -- Si -- two -- H -- six etc. -- the gas of metal hydride [ like ] is mentioned.

[0055] Moreover, as the 2nd mode of the class of raw material for forming the film which controls the above-mentioned anodic oxidation, the gas of an organic compound which does not contain a metal as a component is mentioned. For example, gas, such as ketones, such as hydrocarbon compounds, such as aromatic compounds, such as a pyrene and torr nitril, methane, and ethane, and an acetone, is mentioned. However, if there is no un-arranging in the pore formation by anodic oxidation, especially the class of gas for membrane surface formation will not be restricted.

[0056] using independently as a usage of the raw material for forming the film which controls the above-mentioned anodic oxidation, and Ar, helium and N<sub>2</sub> etc. -- although mixing with gas and using etc. is mentioned, especially if there is no un-arranging in the pore formation by anodic oxidation, it will not be limited to these. [ moreover, ]

[0057] When the 1st raw material furthermore mentioned above is used, the film 14 which controls the above-mentioned anodic oxidation contains a metal. W (CO) When 6 is used as a raw material, the film containing W is formed. On the other hand, the film 14 which controls the above-mentioned anodic oxidation when the 2nd above-mentioned raw material is used turns into film containing carbon. However, in these film, other elements in an ambient atmosphere may be contained as an impurity.

[0058] Furthermore, as the above-mentioned raw material, in aluminum (CH<sub>3</sub>)<sub>3</sub> and the ambient

atmosphere 7 containing  $\text{AlCl}_3$ , aluminum film is formed on the surface of a workpiece, and concavo-convex aluminum is substantially formed in the field of a request of the workpiece which uses aluminum as a principal component by irradiating a corpuscular ray. Therefore, the crevice (the field which is not irradiating the corpuscular ray, or field with few exposures of a corpuscular ray) of aluminum can also be made into a pore formation start point. Therefore, it can be considered that aluminum film acts in this case as film which controls anodic oxidation substantially.

[0059] Next, the corpuscular ray used for this invention is explained. When using a focused ion beam as a corpuscular ray in this invention, as the ion kind, Ga, Si, germanium, Cs, Nb, Cu, etc. which are the liquid metal ion source, O, N, H, helium, Ar which are a source of field ionization gas ion, etc. are mentioned. However, if there is no un-arranging in the pore formation by anodization, especially the ion kind of a focused ion beam will not be restricted.

[0060] However, it is desirable to use Ga as an ion kind of a focused ion beam from the reason of the ease of dealing with it etc. in the ease of treating in fact. Moreover, if the effectiveness of an ion implantation is taken into consideration, an element like noble metals which is hard to anodize may not be desirable as an ion kind of the focused ion beam in this invention. However, in for performing physical deformation of workpiece front faces, such as ion etching on the front face of a workpiece, it is not the limitation in order to form the film 14 for controlling the anodic oxidation mentioned above. Moreover, although it changes according to process terms and conditions, such as an ion kind and acceleration voltage, about the effectiveness by the ion implantation, it is desirable for the element of the ion kind more than 1ppm to exist in the pore formation start point.

[0061] on the other hand -- this invention -- when using an electron beam as a corpuscular ray to kick, it is desirable as the energy to use 1 or more keVs the thing of less than 10 MeV. Therefore, as electronic acceleration voltage, a several kV - about several MV thing is mentioned. However, if there is no un-arranging in the pore formation by anodization, especially the energy and acceleration voltage of an electron beam will not be restricted. However, it is desirable to use 10 or more keVs the thing of 1 or less MeV as energy of an electron beam from the reasons of the repeatability of the configuration of pore etc. in fact. Therefore, 10kV or more 1MV or less is desirable also as acceleration voltage of an electron beam.

[0062] Next, the arrangement pattern of a pore formation start point is explained. It is possible to form a pore formation start point in the location of arbitration in this invention. Moreover, it is not limited especially about spacing and the pattern of a pore formation start point location. However, when actual application is taken into consideration, it will form so that it may become the repeat of the almost same spacing and a pattern by being required to form in the location of the repeat of the almost same spacing and a pattern the nano structure which has pore and pore about a pore formation start point in that case.

[0063] At this time, since there is an inclination for the pattern of pore to become the repeat of a honeycomb-like pattern mostly by self-organizing when the member which uses aluminum as a principal component as a workpiece in the pore formation by anodic oxidation is used, it is desirable to form so that a pore formation start point may become the repeat of a honeycomb-like pattern mostly beforehand. This is desirable especially when it is going to form the structure which has deep pore. However, since the above-mentioned self-organizing does not happen yet when pore is shallow, it is also possible to form so that a pore formation start point may become the repeat of the pattern of configurations of arbitration, such as the shape of a square, mostly.

[0064] Moreover, in the pore formation by anodic oxidation, spacing of pore is controllable by

process terms and conditions, such as the class of electrolytic solution used for anodic oxidation, concentration, temperature and the anodic oxidation electrical-potential-difference impression approach, an electrical-potential-difference value, and time amount, to some extent. Therefore, it is desirable to form a pore formation start point in spacing of the pore expected from process terms and conditions beforehand. For example, it is [0065] experientially between spacing 2R (nm) and the anodic oxidation electrical potential differences  $V_a$  (Volt) of pore.

[Equation 1]

$$2R = 10 + 2V_a \quad (\text{式 } 1)$$

[0066] since there is \*\*\*\*\* -- the maximum access distance (spacing) 2 of a pore formation start point -- as the conditions for  $R_v$  (nm) and the anodic oxidation electrical potential difference  $V_a$  (Volt) -- [0067]

[Equation 2]

$$V_a = (2R_v - 10) / 2 \quad (\text{式 } 2)$$

[0068] It is desirable to apply \*\*\*\*\* conditions, especially the conditions with which a formula 2 is filled in \*\*30% of error range from a formula 2.

[0069] This is desirable especially when it is going to form the structure which has deep pore and deep pore. On the other hand, when the depth of the pore of the workpiece which it is going to form is shallow, the constraint specified from the above-mentioned conditions etc. about spacing of a pore formation start point becomes loose.

[0070] As mentioned above, especially spacing ( $2R_v$ ) of the pore formation start point by this invention is not restricted, but when actual application is taken into consideration, 5nm or more 1000nm or less is desirable.

[0071] Moreover, the intensity distribution of the corpuscular ray which can be used by this invention and which was mentioned above are carrying out Gaussian distribution mostly. therefore -- \*\*\*\* -- the particle-radiation field (namely, diameter of a corpuscular ray) which it can say and is irradiated to each pore formation start point has a desirable method of not lapping with the particle-radiation field (namely, diameter of a corpuscular ray) which irradiates the next pore formation start point. Therefore, as a diameter of the corpuscular ray used for processing in this invention, it is desirable that it is below spacing of a pore formation start point. Therefore, as a diameter of the corpuscular ray used for processing, a thing 500nm or less is desirable.

[0072] (c) Manufacture the structure which has pore 3 in the pore formation start point 2 by performing anodizing to the workpiece 1 in which the pore formation process above-mentioned pore formation start point was formed.

[0073] The outline of the anodic oxidation equipment used for this process is shown in drawing 5. It is the ammeter with which one measures a workpiece and the power source to which in a constant temperature bath and 42 the electrolytic solution and 44 impress a reaction container, and, as for 45, the cathode of Pt plate and 43 impress [ 41 ] an anodic oxidation electrical potential difference among drawing 5, and 46 measures an anodic oxidation current. Although omitted by a diagram, automatic control, the computer to measure are incorporated in the electrical potential difference and the current.

[0074] A workpiece 1 and a cathode 42 are arranged in the electrolytic solution kept constant in temperature with the constant temperature bath, and anodic oxidation is performed by impressing an electrical potential difference between a sample and a cathode from a power source.

[0075] Although oxalic acid, phosphoric acid, a sulfuric acid, a chromic-acid solution, etc. are

mentioned, the electrolytic solution used for anodic oxidation will not be limited especially if there is no un-arranging in the pore formation by anodic oxidation. Moreover, terms and conditions according to each electrolytic solution, such as an anodic oxidation electrical potential difference and temperature, can be suitably set up according to the nano structure to manufacture.

[0076] By pore wide processing in which the above-mentioned nano structure is furthermore dipped into an acid solution (the case of an anodic oxidation alumina for example, phosphoric-acid solution), a pore diameter can be extended suitably. It can consider as the structure which has the pore of a desired path with acid concentration, the processing time, temperature, etc.

[0077] An example (anodic oxidation alumina) of the configuration of the structure which has the pore of this invention is described in <configuration of the nano structure> drawing 2 . A sectional view [ in / drawing 2 (a) and / in drawing 2 (b) / AA line of drawing 2 (a) ] is shown. [ a top view ] As for a workpiece and 3, in drawing 2 , 1 is [ pore (nano hole) and 4 ] barrier layers.

[0078] The structure of this invention is explained here. this structure -- the cylinder-like pore 3 - - having -- each pore 3 -- mutual -- parallel -- and it arranges at equal intervals mostly. Several nm - hundreds of nm and spacing (cell size) 2R of diameter 2r of pore 3 are several nm - about hundreds of nm. the concentration of the electrolytic solution which uses spacing of pore 3, and a diameter for the formation conditions of a pore formation start point, or anodic oxidation, temperature and the anodic oxidation electrical-potential-difference impression approach, an electrical-potential-difference value, and time amount -- they are process terms and conditions, such as subsequent pore wide processing conditions, further -- extent control can be carried out. Moreover, depth d (die length) of pore 3 can be controlled by thickness of anodic oxidation time amount and aluminum etc., for example, while being 10nm - 100 micrometers, it is.

[0079] Moreover, according to the manufacture approach of this invention, as shown not only in a gestalt but in drawing 6 (c) which was shown in drawing 2 (b) and at which pore has stopped on the way like, it can also consider as the structure which has the pore which penetrates a workpiece.

[0080] The nano structure can also be made by using the further above-mentioned nano structure as mold or a mask. By embedding functional materials, such as a metal and a semi-conductor, into pore as an example of formation of such the nano structure, using as mold the nano structure which has pore Although forming quantum wire or forming a quantum dot by vapor-depositing functional materials, such as a metal and a semi-conductor, using the nano structure which has penetration pore as a mask for vacuum evaporation is mentioned, it will not be limited especially if there is no un-arranging in formation of the nano structure.

[0081] Here, (c) of drawing 7 shows the example in which quantum wire was formed, by embedding a filler 6 into pore 3.

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## EXAMPLE

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[Example] An example is raised to below and this invention is explained.

[0083] As shown in preparation drawing 1 (a) of an example 1 (a) workpiece, what performed mirror plane processing for the front face of aluminum plate of 99.99% of purity by electric-field polish in the mixed solution of perchloric acid and ethanol as a workpiece was prepared.

[0084] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 1 (b), the pore formation start point 2 was formed in the workpiece. The ion kind of

focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here.

[0085] First, the location which forms a pore formation start point was defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, using the focused ion beam of 30nm of ion beam \*\*\*\*, and ion current abbreviation 3pA, as shown in drawing 4 (a), the pore formation start point was formed by irradiating a focused ion beam in the shape of a dot at a workpiece, as it becomes the repeat of the pattern of a honeycomb mostly at intervals of about 100nm. At this time, the residence time of the focused ion beam in each dot location was about 10 msec(s).

[0086] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 40 -- it was referred to as V.

[0087] next, a workpiece -- after anodizing -- 5wt(s)% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0088] Evaluation (structure observation)

When the workpiece was observed in FE-SEM (field emission scanning electron microscope), a pole diameter is about 50nm, pore spacing is about 100nm, and, as for each pore, it was checked that the repeat of a honeycomb-like pattern is formed mostly and the high nano structure of the regularity of pore is formed.

[0089] As shown in preparation drawing 3 (b) of an example 2 (a) workpiece, what formed aluminum film with a thickness of about 200nm with resistance heating vacuum deposition was prepared on the quartz substrate as a workpiece.

[0090] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 1 (b), the pore formation start point was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here. The location which forms a pore formation start point was first defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, using the focused ion beam of 30nm of ion beam \*\*\*\*, and ion current abbreviation 3pA, as shown in drawing 4 (b), the pore formation start point was formed by irradiating a focused ion beam in the shape of a dot at a workpiece, as it becomes the repeat of the pattern of forward four square shapes mostly at intervals of about 60nm. At this time, the residence time of the focused ion beam in each dot location was about 100 msec(s).

[0091] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M sulfuric-acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 25 -- it was referred to as V.

[0092] next, a workpiece -- after anodizing -- 5wt(s)% -- the path of pore was extended by dipping between 20min into a phosphoric-acid solution.

[0093] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pole diameter is about 40nm, pore spacing is about 60nm, and it was checked that each pore is mostly formed by the repeat of a forward 4 square-shape-like pattern, and the high nano structure of the regularity of pore is formed.

[0094] The same workpiece as the preparation example 1 of an example 3 (a) workpiece was

prepared.

[0095] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 1 (b), the pore formation start point was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here. The location which forms a pore formation start point was first defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, the pore formation start point was formed in the intersection of each Rhine by irradiating a focused ion beam at the shape of Rhine so that it may become the repeat of Rhine almost parallel to a direction which is different 60 degrees to previous Rhine after irradiating a focused ion beam at the shape of Rhine so that it may become the repeat of Rhine almost parallel at intervals of about 100nm, as shown in drawing 4 (c) using the focused ion beam of 30nm of ion beam \*\*\*\*, and ion current abbreviation 3pA at intervals of about 100nm. A scanning speed and the count of a scan were adjusted so that the sum total of the residence time of the focused ion beam in the intersection of Rhine might be set to about 10 msec(s) at this time.

[0096] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 50 -- it was referred to as V.

[0097] next, a workpiece -- after anodizing -- 5wt(s)% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0098] Evaluation (structure observation) .

When the workpiece was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 115nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed.

[0099] As shown in preparation drawing 8 (a) of an example 4 (a) workpiece, after forming Ti film used as about 50nm pore trailer material 15 by the spatter and forming a base 13 on the Si substrate 16 What formed about 500nm aluminum film 12 with resistance heating vacuum deposition, and formed about 20nm Pt film which is the conductive film 17 in a spatter about SiO<sub>2</sub> about 20nm film which is the insulator film 18 as a membrane surface 14 further by the spatter was prepared as a workpiece 1.

[0100] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 8 (b), the pore formation start point was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here. The location which forms a pore formation start point was first defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, using the focused ion beam of 50nm of ion beam \*\*\*\*, and ion current abbreviation 60pA, as shown in drawing 11 (a), the pore formation start point was formed by irradiating a focused ion beam in the shape of a dot at a workpiece, as it becomes the repeat of the pattern of a honeycomb mostly at intervals of about 150nm. At this time, the residence time of the focused ion beam in each dot location was about 30 msec(s).

[0101] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed. the acid electrolytic solution -- a 0.3M phosphate water solution -- using -- a constant temperature bath -- a solution --

3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 70 -- it was referred to as V. It was able to check that anodic oxidation had reached to the pore \*\*\*\* member by reduction in a current value here at the time of anodic oxidation.

[0102] next, a workpiece -- after anodizing -- 5wt(s)% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution (.) (refer to drawing 8 (c))

[0103] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, the pole diameter in a membrane surface is [ about 70nm and pore spacing of the pole diameter in about 50nm and the alumina film ] about 150nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed. Moreover, when electric measurement of a workpiece was performed, it was checked that surface Pt film is insulated by holding conductivity and coincidence between surface Pt film and Ti film which is a pore terminal point member.

[0104] Example 5 this example is an example which produced the nano structure which has penetration pore by removing parts other than the part which has pore.

[0105] (a) Using the same approach as (a) and (b) of preparation of a workpiece, and the formation process example 1 of (b) pore formation start point, after preparing a workpiece, the pore formation start point was formed in the workpiece.

[0106] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 40 -- it was referred to as V.

[0107] (d) The removal process of parts other than the part which has the removal process pore of parts other than the part which has pore is shown in drawing 6 (a) - (c). The part of the bulk 11 of aluminum of a workpiece was removed by dipping the nano structure as first shown in drawing 6 (a) in the HgCl<sub>2</sub> saturated solution ( drawing 6 (b)). next, a workpiece -- 5wt(s)% -- while removing the barrier layer 4 by dipping between 30min into a phosphoric-acid solution, by extending the path of pore, the nano structure which has the penetration pore 5 was produced ( drawing 6 (c)).

[0108] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 100nm, and it was checked that each penetration pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of penetration pore is formed.

[0109] Example 6 this example is an example which was filled up with the metal in pore and produced the nano structure (quantum wire), using as mold the nano structure which has the pore formed by anodic oxidation.

[0110] (a) As shown in preparation drawing 7 (a) of a workpiece, after forming Ti film used as pore trailer material 15 with a thickness of about 50nm by the spatter and forming a base 13 on the Si substrate 16, what formed the aluminum film 12 with a thickness of about 500nm with resistance heating vacuum deposition further was prepared as a workpiece 1.

[0111] (b) The pore formation start point was formed in the workpiece using the same approach as (b) of an example 1 except the residence time of the focused ion beam in formation process each dot location of a pore formation start point being about 100 msec(s).

[0112] (c) The path of pore was extended after forming pore in a workpiece using the same

approach as (c) of the formation process example 1 of pore ( drawing 7 (b) ). It was able to check that anodic oxidation had reached to pore trailer material by reduction in a current value here at the time of anodic oxidation.

[0113] (d) When the metal packer into pore performed nickel metal electrodeposition more next, it was filled up with the filler 6 in pore ( drawing 7 (c) ). nickel was deposited in the nano hole by nickel restoration dipping and electrodepositing it with the counterelectrode of nickel, in the electrolytic solution which consists of H<sub>3</sub>BO<sub>3</sub> of NiSO<sub>4</sub> and 0.5M of 0.14M.

[0114] Evaluation (structure observation)

When the workpiece before nickel restoration was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 100nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed. Moreover, it was checked that pore has reached to pore trailer material, and the die length of pore was controlled by arranging pore trailer material.

[0115] When the workpiece after nickel \*\*\*\* was furthermore observed in FE-SEM, pore is filled up with nickel and the quantum wire which consists of nickel of about 50nm of sizes was formed.

[0116] The example 1 of the one example comparison of a comparison produced the nano structure by the same approach as an example 1 except having not performed the formation process of (b) pore formation start point in the example 1.

[0117] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, the pole diameter was 30-50nm, pore spacing was 90-100nm, each pore was formed at random and the regularity of pore was low.

[0118] As shown in preparation drawing 1 (a) of an example 7 (a) workpiece, what performed mirror plane processing for the front face of aluminum plate of 99.99% of purity as a workpiece by electrolytic polishing in the inside of the mixed solution of perchloric acid and ethanol was prepared.

[0119] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 1 (b), the pore formation start point was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here.

[0120] The location which forms a pore formation start point was first defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, using the electron beam with a beam diameter of about 10nm, as shown in drawing 4 (a), the pore formation start point was formed by irradiating an electron beam in the shape of a dot at a workpiece, as it becomes the repeat of the pattern of a honeycomb mostly at intervals of about 100nm (2Rv).

[0121] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 40 -- it was referred to as V.

[0122] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0123] Evaluation (structure observation)

When the workpiece was observed in FE-SEM (field emission scanning electron microscope), a pole diameter is about 50nm, pore spacing is about 100nm, and, as for each pore, it was checked



that the repeat of a honeycomb-like pattern is formed mostly and the high nano structure of the regularity of pore is formed.

[0124] As shown in preparation drawing 3 (b) of an example 8 (a) workpiece, what formed the aluminum film 12 with a thickness of about 200nm with resistance heating vacuum deposition was prepared on the quartz substrate 13 as a workpiece.

[0125] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 1 (b), the pore formation start point was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here. The location which forms a pore formation start point was first defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, using the electron beam with a beam diameter of about 10nm, as shown in drawing 4 (b), the pore formation start point was formed by irradiating an electron beam in the shape of a dot at a workpiece, as it becomes the repeat of the pattern of forward four square shapes mostly at intervals of about 60nm (2Rv).

[0126] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M sulfuric-acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 25 -- it was referred to as V.

[0127] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 20min into a phosphoric-acid solution.

[0128] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pore diameter is about 40nm, pore spacing is about 60nm, and it was checked that each pore is mostly formed by the repeat of a forward 4 square-shape-like pattern, and the high nano structure of the regularity of pore is formed.

[0129] The same workpiece as the preparation example 7 of an example 9 (a) workpiece was prepared.

[0130] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 1 (b), the pore formation start point was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here. The location which forms a pore formation start point was first defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, the pore formation start point was formed in the intersection of each Rhine by irradiating an electron beam at the shape of Rhine so that it may become the repeat of Rhine almost parallel to a direction which is different 60 degrees to previous Rhine after irradiating an electron beam at the shape of Rhine so that it may become the repeat of Rhine almost parallel at intervals of about 100nm, as shown in drawing 4 (c) using an electron beam with a beam diameter of about 30nm at intervals of about 100nm.

[0131] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 50 -- it was referred to as V.

[0132] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0133] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 115nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed.

[0134] As shown in a detail at (a) of preparation drawing 8 of an example 10 (a) workpiece After forming Ti film used as a pore terminal point member 15 with a thickness of about 50nm by the spatter and forming a base 13 on the Si substrate 16 SiO<sub>2</sub> with a thickness of about 20nm which the aluminum film 12 with a thickness of about 500nm is formed with resistance heating vacuum deposition, and is the insulator film 18 as a membrane surface 14 further What formed Pt film with a thickness of about 20nm which is the conductive film 17 in a spatter about the film by the spatter was prepared as a workpiece 1.

[0135] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 8 (b), the pore formation start point 2 was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here. The location which forms a pore formation start point was first defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, using the electron beam of 10nm of ion beam \*\*\*\*, as shown in drawing 11 (a), the pore formation start point was formed by irradiating an electron beam in the shape of a dot at a workpiece, as it becomes the repeat of the pattern of a honeycomb mostly at intervals of about 150nm.

[0136] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed. the acid electrolytic solution -- a 0.3M phosphate water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 70 -- it was referred to as V. It was able to check that anodic oxidation had reached to the pore terminal point member by reduction in a current value here at the time of anodic oxidation.

[0137] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution (.) (refer to drawing 8 (c))

[0138] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, the pole diameter in a membrane surface is [ about 70nm and pore spacing of the pole diameter in about 50nm and the alumina film ] about 150nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed. Moreover, when electric measurement of a workpiece was performed, it was checked that surface Pt film is insulated by holding conductivity and coincidence between surface Pt film and Ti film which is a pore terminal point member.

[0139] Example 11 this example is an example which manufactured the structure which has the penetrated pore. (a) The same approach as (a) and (b) of an example 7 was used for preparation of a workpiece, and the formation process of (b) pore formation start point.

[0140] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 1 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 40 -- it was referred to as V.

[0141] (d) The removal process of parts other than the part which has the removal process pore of parts other than the part which has pore is shown in (a) - (c) of drawing 6 . The part of the bulk 11 of aluminum of a workpiece was removed by dipping the nano structure as first shown in

(a) of drawing 6 in the  $\text{HgCl}_2$  saturated solution ((b) of drawing 6 ). next, a workpiece -- 5wt(s)% -- while removing the barrier layer 4 by dipping between 30min into a phosphoric-acid solution, by extending the path of pore, the nano structure which has the penetration pore 5 was manufactured ((c) of drawing 6 ).

[0142] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 100nm, and it was checked that each penetration pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of penetration pore is formed.

[0143] Example 12 this example is an example which was filled up with the metal in pore as mold formed by anodic oxidation, and manufactured the nano structure (quantum wire).

[0144] (a) As shown in a detail at (a) of preparation drawing 7 of a workpiece, after forming Ti film used as a pore terminal point member 15 with a thickness of about 50nm by the sputter and forming a base 13 on the Si substrate 16, what formed the aluminum film 12 with a thickness of about 500nm with resistance heating vacuum deposition further was prepared as a workpiece 1.

[0145] (b) The pore formation start point was formed in the workpiece using the same approach as (b) of the formation process example 7 of a pore formation start point.

[0146] (c) The path of pore was extended after forming pore in a workpiece using the same approach as (c) of the formation process example 7 of pore ((b) of drawing 7 ). It was able to check that anodic oxidation had reached to the pore terminal point member by reduction in a current value here at the time of anodic oxidation.

[0147] (d) When the metal packer into pore next performed nickel metal electrodeposition, it was filled up with the filler 6 in pore ((c) of drawing 7 ). nickel was deposited in the nano hole by nickel restoration dipping and electrodepositing it with the counterelectrode of nickel, in the electrolytic solution which consists of  $\text{H}_3\text{BO}_3$  of  $\text{NiSO}_4$  and 0.5M of 0.14M.

[0148] Evaluation (structure observation)

When the workpiece before nickel restoration was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 100nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed. Moreover, it was checked that pore has reached to a pore terminal point member, and the die length of pore was controlled by arranging a pore terminal point member.

[0149] When the workpiece after nickel restoration was furthermore observed in FE-SEM, pore is filled up with nickel and the quantum wire which consists of nickel of about 50nm of sizes was formed.

[0150] As shown in example 13(a) workpiece preparation drawing 9 (a), what performed mirror plane processing for the front face of aluminum plate of 99.99% of purity by electric-field polish in the mixed solution of perchloric acid and ethanol as a workpiece was prepared.

[0151] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 9 (b), the pore formation start point was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here.

[0152] The location which forms a pore formation start point was first defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, pyrene gas was introduced in focusing ion beam machining equipment as gas for membrane surface formation. Furthermore, the pore formation start point was formed using the focused ion beam of 30nm of ion beam \*\*\*\*, and ion current abbreviation 3pA by irradiating a

focused ion beam so that the non-irradiating location of a focused ion beam may become the repeat of the pattern of a honeycomb mostly at intervals of about 150nm, as shown in drawing 10 (a). The membrane surface containing C is formed in the exposure location of a focused ion beam at this time.

[0153] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M phosphate water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 70 -- it was referred to as V.

[0154] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0155] Evaluation (structure observation)

When the workpiece was observed in FE-SEM (field emission scanning electron microscope), a pole diameter is about 50nm, pore spacing is about 150nm, and, as for each pore, it was checked that the repeat of a honeycomb-like pattern is formed mostly and the high nano structure of the regularity of pore is formed.

[0156] As shown in example 14(a) workpiece preparation drawing 3 (b), what formed about 200nm aluminum film 12 with resistance heating vacuum deposition was prepared on the quartz substrate 13 as a workpiece.

[0157] (b) The focused ion beam exposure was performed to the workpiece using the formation process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 9 (b), the pore formation start point was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here.

[0158] First, the location which forms a pore formation start point was defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, pyrene gas was introduced in focusing ion beam machining equipment as gas for membrane surface formation. Furthermore, the pore formation start point was formed using the focused ion beam of 30nm of ion beam \*\*\*\*, and ion current abbreviation 3pA by irradiating a focused ion beam so that the non-irradiating location of a focused ion beam may become the repeat of the pattern of forward four square shapes mostly at intervals of about 150nm, as shown in drawing 10 (b). The membrane surface containing C is formed in the exposure location of a focused ion beam at this time.

[0159] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 60 -- it was referred to as V.

[0160] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0161] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 150nm, and it was checked that each pore is formed by the repeat of a \*\*\*\* right 4 square-shape-like pattern, and the high nano structure of the regularity of pore is formed.

[0162] The same workpiece as the example 15(a) workpiece preparation example 13 was prepared.

[0163] (b) The focused ion beam exposure was performed to the workpiece using the formation

process focusing ion beam machining equipment of a pore formation start point, and as shown in drawing 9 (b), the pore formation start point was formed in the workpiece. The ion kind of focusing ion beam machining equipment is Ga, and acceleration voltage is 30kV here.

[0164] First, the location which forms a pore formation start point was defined using the secondary electron observation function of focusing ion beam machining equipment attachment. Next, W(CO) 6 gas was introduced in focusing ion beam machining equipment as gas for membrane surface formation. Next, the focused ion beam of 30nm of ion beam \*\*\*\* and ion current abbreviation 3pA is used. After irradiating a focused ion beam in the shape of Rhine so that it may become the repeat of almost parallel Rhine at intervals of about 150nm as shown in drawing 10 (c) The pore formation start point was formed in the field surrounded by each Rhine by irradiating a focused ion beam in the shape of Rhine so that it may become the repeat of Rhine almost parallel to a direction which is different 60 degrees to previous Rhine at intervals of about 150nm. The membrane surface containing W is formed in the exposure location of a focused ion beam at this time.

[0165] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M phosphate water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 80 -- it was referred to as V.

[0166] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0167] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 170nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed.

[0168] Example 16 this example is an example which manufactured the nano structure which has penetration pore by removing parts other than the part which has pore.

[0169] (a) Using the same approach as (a) and (b) of the formation process example 13 of workpiece preparation and (b) pore formation start point, after preparing a workpiece, the pore formation start point was formed in the workpiece.

[0170] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 70 -- it was referred to as V.

[0171] (d) The removal process of parts other than the part which has the removal process pore of parts other than the part which has pore is shown in (a) - (c) of drawing 6 . The membrane surface 14 was removed by carrying out Ar ion etching of the workpiece as first shown in drawing 9 (c) ((a) of drawing 6 ). Next, the part of the bulk 11 of aluminum of a workpiece was removed by dipping a workpiece in the HgCl<sub>2</sub> saturated solution ((b) of drawing 6 ). next, a workpiece -- 5wt(s)% -- while removing the barrier layer 4 by dipping between 30min into a phosphoric-acid solution, by extending the path of pore, the nano structure which has the penetration pore 5 was manufactured ((c) of drawing 6 ).

[0172] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 150nm, and it was checked that each penetration pore is mostly formed by the repeat of a

honeycomb-like pattern, and the high nano structure of the regularity of penetration pore is formed.

[0173] Example 17 this example is an example which was filled up with the metal in pore and manufactured the nano structure (quantum wire), using as mold the nano structure which has the pore formed by anodic oxidation.

[0174] (a) As shown in a detail at (a) of workpiece preparation drawing 7, after forming Ti film used as pore trailer material 15 with a thickness of about 50nm by the spatter and forming a base 13 on the Si substrate 16, what formed the aluminum film 12 with a thickness of about 500nm with resistance heating vacuum deposition further was prepared as a workpiece 1.

[0175] (b) The pore formation start point was formed in the workpiece using the same approach as (b) of the formation process example 13 of a pore formation start point.

[0176] (c) The path of pore was extended after forming pore in a workpiece using the same approach as (c) of the formation process example 13 of pore ((b) of drawing 7). It was able to check that anodic oxidation had reached to pore trailer material by reduction in a current value here at the time of anodic oxidation.

[0177] (d) When the metal packer into pore performed nickel metal electrodeposition more next, it was filled up with the filler 6 in pore ((c) of drawing 7). nickel was deposited in the nano hole by nickel restoration dipping and electrodepositing it with the counterelectrode of nickel, in the electrolytic solution which consists of 0.14M NiSO<sub>4</sub> and 0.5M H<sub>3</sub>BO<sub>3</sub>.

[0178] Evaluation (structure observation)

When the workpiece before nickel restoration was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 150nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed. Moreover, it was checked that pore has reached to pore trailer material, and the die length of pore was controlled by arranging pore trailer material.

[0179] When the workpiece after nickel restoration was furthermore observed in FE-SEM, pore is filled up with nickel and the quantum wire which consists of nickel of about 50nm of sizes was formed.

[0180] As shown in example 18(a) workpiece preparation drawing 9 (a), what performed mirror plane processing for the front face of aluminum plate of 99.99% of purity by electric-field polish in the mixed solution of perchloric acid and ethanol as a workpiece was prepared.

[0181] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 9 (b), the pore formation start point was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here.

[0182] First, the location which forms a pore formation start point was defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, pyrene gas was introduced in electron beam irradiation equipment as gas for membrane surface formation. Furthermore, the pore formation start point was formed using the electron beam with a beam diameter of about 10nm by irradiating an electron beam so that the non-irradiating location of an electron beam may become the repeat of the pattern of a honeycomb mostly at intervals of about 150nm, as shown in drawing 10 (a). The membrane surface containing C is formed in the exposure location of an electron beam at this time.

[0183] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M phosphate water solution -- using -- a constant

temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 70 -- it was referred to as V.

[0184] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0185] Evaluation (structure observation)

When the workpiece was observed in FE-SEM (field emission scanning electron microscope), a pole diameter is about 50nm, pore spacing is about 150nm, and, as for each pore, it was checked that the repeat of a honeycomb-like pattern is formed mostly and the high nano structure of the regularity of pore is formed.

[0186] As shown in example 19(a) workpiece preparation drawing 9 (a), what formed aluminum film with a thickness of about 200nm with resistance heating vacuum deposition was prepared on the quartz substrate as a workpiece.

[0187] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 9 (b), the pore formation start point was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here.

[0188] First, the location which forms a pore formation start point was defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, pyrene gas was introduced in electron beam irradiation equipment as gas for membrane surface formation. Furthermore, the pore formation start point was formed using the electron beam with a beam diameter of about 10nm by irradiating an electron beam so that the non-irradiating location of an electron beam may become the repeat of the pattern of forward four square shapes mostly at intervals of about 150nm, as shown in drawing 10 (b). The membrane surface containing C is formed in the exposure location of an electron beam at this time.

[0189] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 60 -- it was referred to as V.

[0190] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0191] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 150nm, and it was checked that each pore is mostly formed by the repeat of a forward 4 square-shape-like pattern, and the high nano structure of the regularity of pore is formed.

[0192] The same workpiece as the example 20(a) workpiece preparation example 18 was prepared.

[0193] (b) The electron beam exposure was performed to the workpiece using the formation process electron beam irradiation equipment of a pore formation start point, and as shown in drawing 9 (b), the pore formation start point was formed in the workpiece. The acceleration voltage of electron beam irradiation equipment is 200kV here.

[0194] First, the location which forms a pore formation start point was defined using the secondary electron observation function of electron beam irradiation equipment attachment. Next, W(CO) 6 gas was introduced in electron beam irradiation equipment as gas for membrane surface formation. Next, the pore formation start point was formed in the field surrounded by each Rhine by irradiating an electron beam at the shape of Rhine so that it may become the

repeat of Rhine almost parallel to a direction which is different 60 degrees to previous Rhine after irradiating an electron beam at the shape of Rhine so that it may become the repeat of Rhine almost parallel at intervals of about 150nm, as shown in drawing 10 (c) using an electron beam with a beam diameter of about 10nm at intervals of about 150nm. The membrane surface containing W is formed in the exposure location of an electron beam at this time.

[0195] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M phosphate water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 80 -- it was referred to as V.

[0196] next, a workpiece -- after [ anodizing ] and 5wt% -- the path of pore was extended by dipping between 30min into a phosphoric-acid solution.

[0197] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 170nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed.

[0198] Example 21 this example is an example which manufactured the nano structure which has penetration pore by removing parts other than the part which has pore.

[0199] (a) Using the same approach as (a) and (b) of the formation process example 18 of workpiece preparation and (b) pore formation start point, after preparing a workpiece, the pore formation start point was formed in the workpiece.

[0200] (c) Anodizing was performed to the workpiece using the anodic oxidation equipment of formation process drawing 5 of pore, and the pore object was formed as shown in drawing 9 (c). the acid electrolytic solution -- a 0.3M oxalic acid water solution -- using -- a constant temperature bath -- a solution -- 3 degrees C -- holding -- an anodic oxidation electrical potential difference -- about 70 -- it was referred to as V.

[0201] (d) The removal process of parts other than the part which has the removal process pore of parts other than the part which has pore is shown in (a) - (c) of drawing 6 . The membrane surface 14 was removed by carrying out Ar ion etching of the workpiece as first shown in (c) of drawing 9 ((a) of drawing 6 ). Next, the part of the bulk 11 of aluminum of a workpiece was removed by dipping a workpiece in the HgCl<sub>2</sub> saturated solution ((b) of drawing 6 ). next, a workpiece -- 5wt(s)% -- while removing the barrier layer 4 by dipping between 30min into a phosphoric-acid solution, by extending the path of pore, the nano structure which has the penetration pore 5 was manufactured ((c) of drawing 6 ).

[0202] Evaluation (structure observation)

When the workpiece was observed in FE-SEM, a pore diameter is about 50nm, pore spacing is about 150nm, and it was checked that each penetration pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of penetration pore is formed.

[0203] Example 22 this example is an example which was filled up with the metal in pore and manufactured the nano structure (quantum wire), using as mold the nano structure which has the pore formed by anodic oxidation.

[0204] (a) As shown in a detail at (a) of workpiece preparation drawing 7 , after forming Ti film used as pore trailer material 15 with a thickness of about 50nm by the spatter and forming a base 13 on the Si substrate 16, what formed the aluminum film 12 with a thickness of about 500nm with resistance heating vacuum deposition further was prepared as a workpiece 1.

[0205] (b) The pore formation start point was formed in the workpiece using the same approach



as (b) of the formation process example 18 of a pore formation start point.

[0206] (c) The path of pore was extended after forming pore in a workpiece using the same approach as (c) of the formation process example 18 of pore ((b) of drawing 7 ). It was able to check that anodic oxidation had reached to pore trailer material by reduction in a current value here at the time of anodic oxidation.

[0207] (d) When the metal packer into pore performed nickel metal electrodeposition more next, it was filled up with the filler 6 in pore ((c) of drawing 7 ). nickel restoration -- 0.14MNiSO<sub>4</sub> and 0.5MHBO<sub>3</sub> from -- nickel was deposited in the nano hole by being dipped and electrodeposited with the counterelectrode of nickel in the becoming electrolytic solution.

[0208] Evaluation (structure observation)

When the workpiece before nickel restoration was observed in FE-SEM, a pole diameter is about 50nm, pore spacing is about 150nm, and it was checked that each pore is mostly formed by the repeat of a honeycomb-like pattern, and the high nano structure of the regularity of pore is formed. Moreover, it was checked that pore has reached to pore trailer material, and the die length of pore was controlled by arranging pore trailer material.

[0209] When the workpiece after nickel restoration was furthermore observed in FE-SEM, pore is filled up with nickel and the quantum wire which consists of nickel of about 50nm of sizes was formed.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is process drawing showing an example of the manufacture approach of the nano structure of this invention.

[Drawing 2] It is the schematic diagram showing an example of the nano structure of this invention.

[Drawing 3] It is the explanatory view showing an example of the gestalt of the workpiece of this invention.

[Drawing 4] It is the explanatory view showing an example of formation of the pore formation start point by the particle radiation of this invention.

[Drawing 5] It is the schematic diagram showing anodic oxidation equipment.

[Drawing 6] It is process drawing showing an example of the manufacture approach of the nano structure which has the through tube of this invention.

[Drawing 7] It is process drawing showing an example of the manufacture approach of the nano structure which has a filler in the pore of this invention.

[Drawing 8] It is process drawing showing an example of the manufacture approach of the nano structure of this invention.

[Drawing 9] It is process drawing showing an example of the manufacture approach of the nano structure of this invention.

[Drawing 10] It is the explanatory view showing an example of formation of the pore formation start point by the particle radiation of this invention.

[Drawing 11] It is the explanatory view showing an example of formation of the pore formation start point by the particle radiation of this invention.

[Description of Notations]

1 Workpiece

2 Pore Formation Start Point

3 Pore  
4 Barrier Layer  
5 Penetration Pore  
6 Filler  
10 Corpuscular Ray  
11 Bulk of Aluminum  
12 Film of Aluminum  
13 Base  
14 Membrane Surface  
15 Pore Terminal Point Member  
16 Substrate  
17 Conductive Film  
18 Insulator Film  
31 Dot Exposure Location  
32 Rhine Exposure Location  
33 Rhine Intersection  
41 Constant Temperature Bath  
42 Cathode  
43 Electrolytic Solution  
44 Reaction Container  
45 Power Source  
46 Ammeter

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## CLAIMS

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[Claim(s)]

[Claim 1] The manufacture approach of the pore characterized by having the process which irradiates a corpuscular ray at a workpiece, and the process which forms pore in said workpiece by anodizing the workpiece which irradiated said corpuscular ray.

[Claim 2] The manufacture approach of the pore according to claim 1 characterized by said corpuscular ray being a charged particle beam.

[Claim 3] The manufacture approach of the pore according to claim 1 or 2 characterized by said corpuscular ray being a focused ion beam or an electron beam.

[Claim 4] The manufacture approach of pore given in claim 1 characterized by irradiating said corpuscular ray at two or more parts of a workpiece thru/or one term of 3.

[Claim 5] The manufacture approach of pore given in claim 1 characterized by carrying out the multiple-times exposure of said corpuscular ray at the same part of said workpiece thru/or one term of 3.

[Claim 6] The manufacture approach of pore given in claim 1 characterized by changing the amount of the corpuscular ray to irradiate and irradiating said corpuscular ray with the location which irradiates said workpiece thru/or one term of 3.

[Claim 7] The process which irradiates said corpuscular ray is the manufacture approach of pore given in claim 1 characterized by being the process which removes said film alternatively thru/or one term of 6 by irradiating said corpuscular ray at the film which controls the anodic oxidation arranged on the front face of said workpiece.

[Claim 8] The process which irradiates said corpuscular ray is the manufacture approach of pore

given in claim 1 characterized by being the process which forms in the front face of said workpiece the film which controls anodic oxidation alternatively from the raw material contained in the ambient atmosphere which surround said workpiece thru/or one term of 6.

[Claim 9] The manufacture approach of pore given in claim 1 characterized by the diameter of the corpuscular ray which irradiates said workpiece being 500nm or less thru/or one term of 8.

[Claim 10] The manufacture approach of pore given in claim 2 characterized by the elements of the ion kind used for said focused ion beam being elements other than noble metals thru/or one term of 9.

[Claim 11] The manufacture approach of the pore according to claim 10 characterized by pouring into said workpiece the element of the ion kind used for said focused ion beam more than 1ppm.

[Claim 12] The manufacture approach of pore given in claim 1 which is the member to which said workpiece uses aluminum as a principal component thru/or one term of 11.

[Claim 13] The manufacture approach of pore given in claim 7 whose film which controls said anodic oxidation is an insulator thru/or one term of 12.

[Claim 14] The manufacture approach of pore given in claim 7 which is the metal with which the film which controls said anodic oxidation contains Nb, Ti, Ta, Zr, W, or Hf thru/or one term of 12.

[Claim 15] The manufacture approach of pore given in claim 7 which the film which controls said anodic oxidation becomes from the conductive film formed the insulator film and on it thru/or one term of 14.

[Claim 16] The manufacture approach of pore given in claim 8 to which the raw material contained in the ambient atmosphere which surround said workpiece is characterized by being a metal carbonyl, metal hydride, a metal halogenide, or an organic compound thru/or one term of 15.

[Claim 17] The manufacture approach of the pore according to claim 16 characterized by said organic compound being an organometallic compound.

[Claim 18] Pore manufactured by the approach of claim 1 thru/or either of 17.

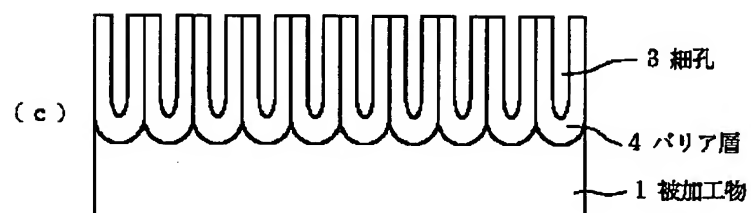
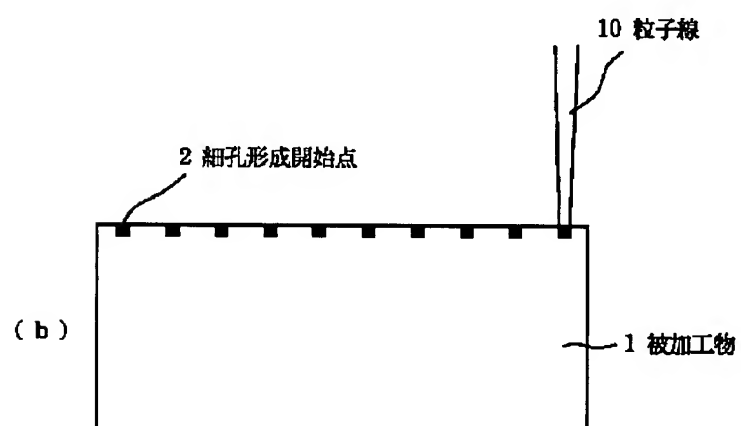
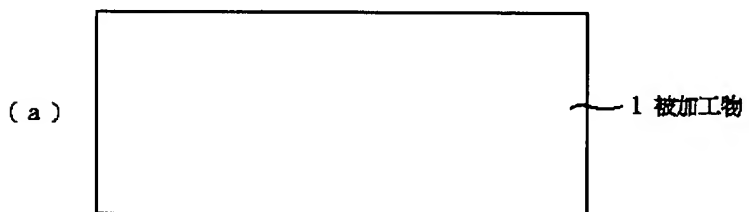
[Claim 19] The structure which has the pore manufactured by the approach of claim 1 thru/or either of 17.

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## DRAWINGS

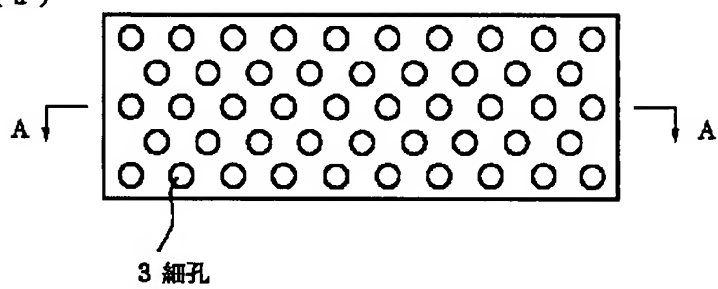
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### [Drawing 1]

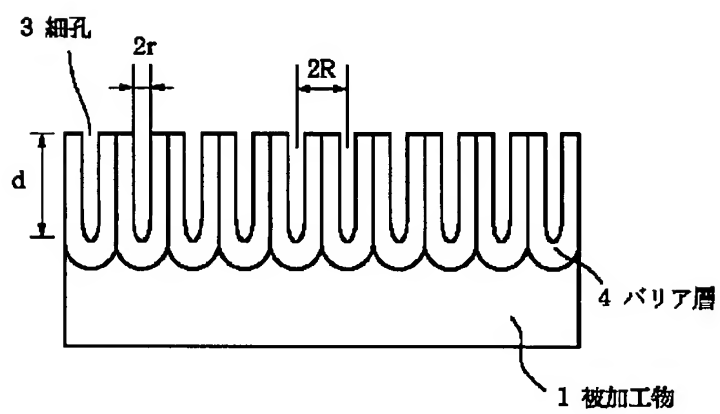


[Drawing 2]

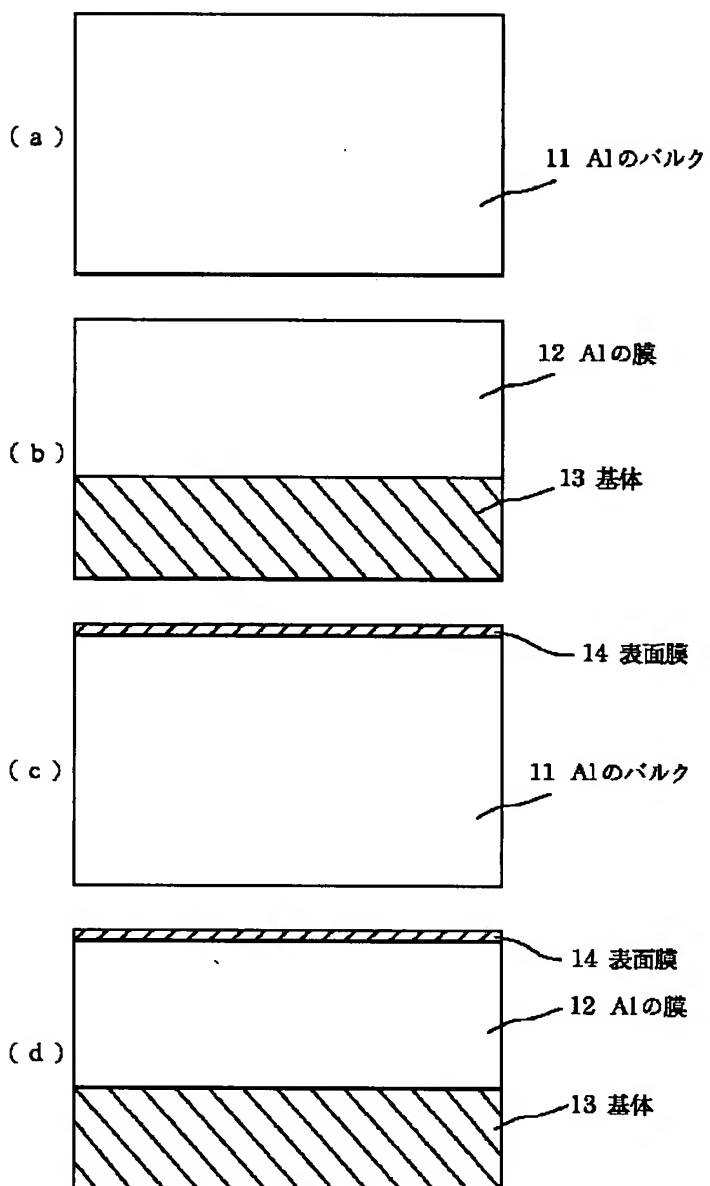
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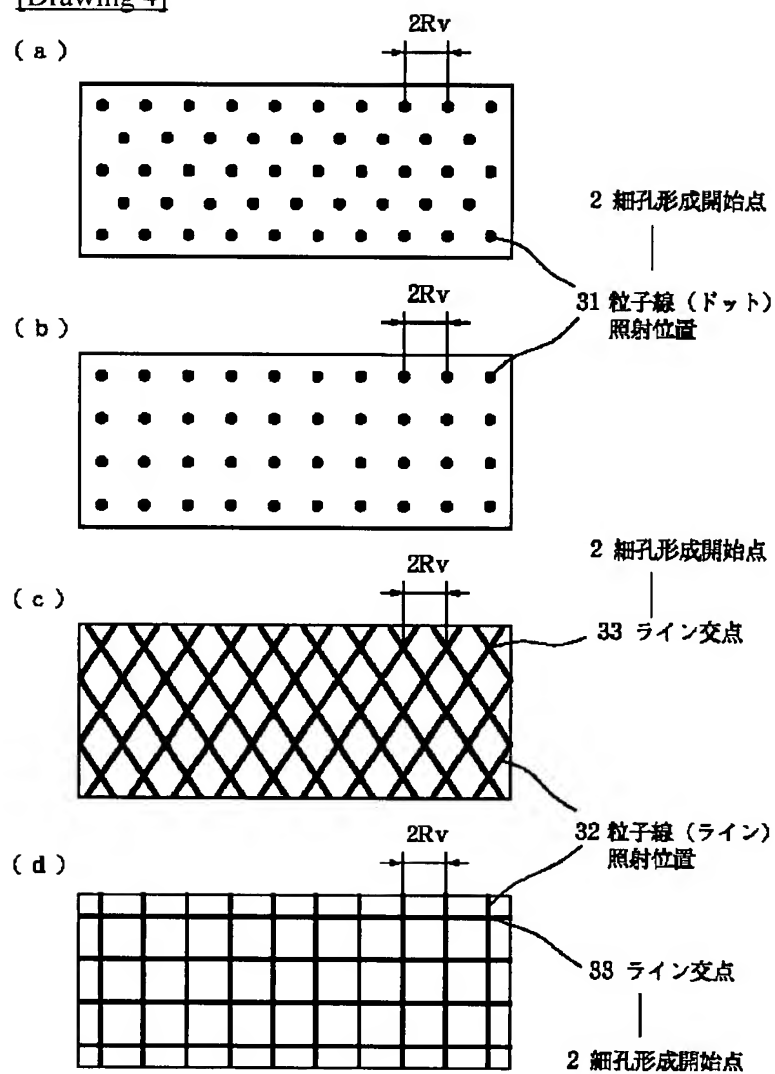
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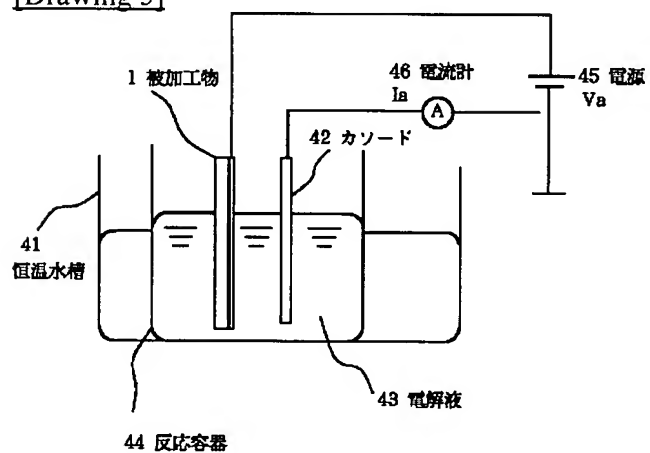
[Drawing 3]



[Drawing 4]



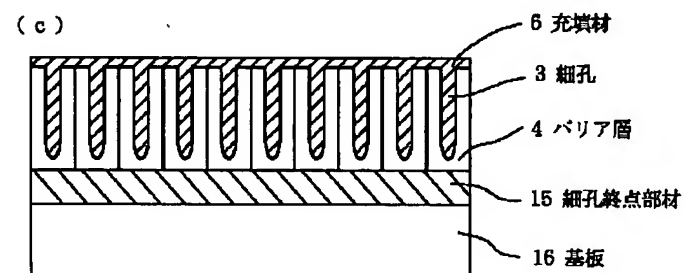
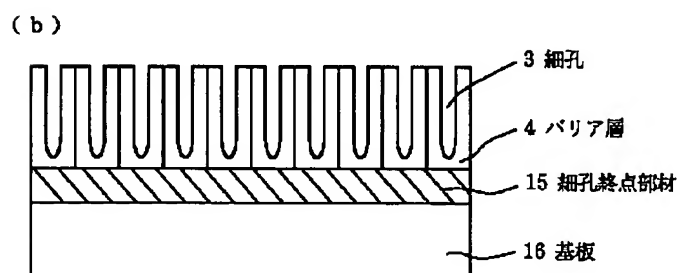
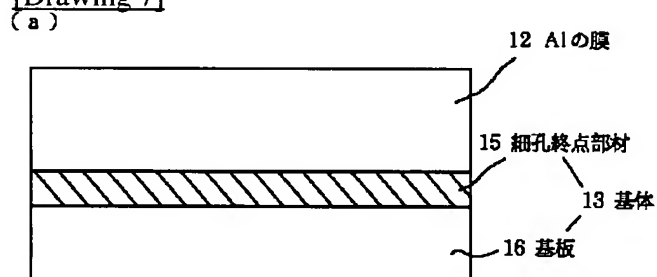
[Drawing 5]



[Drawing 6]

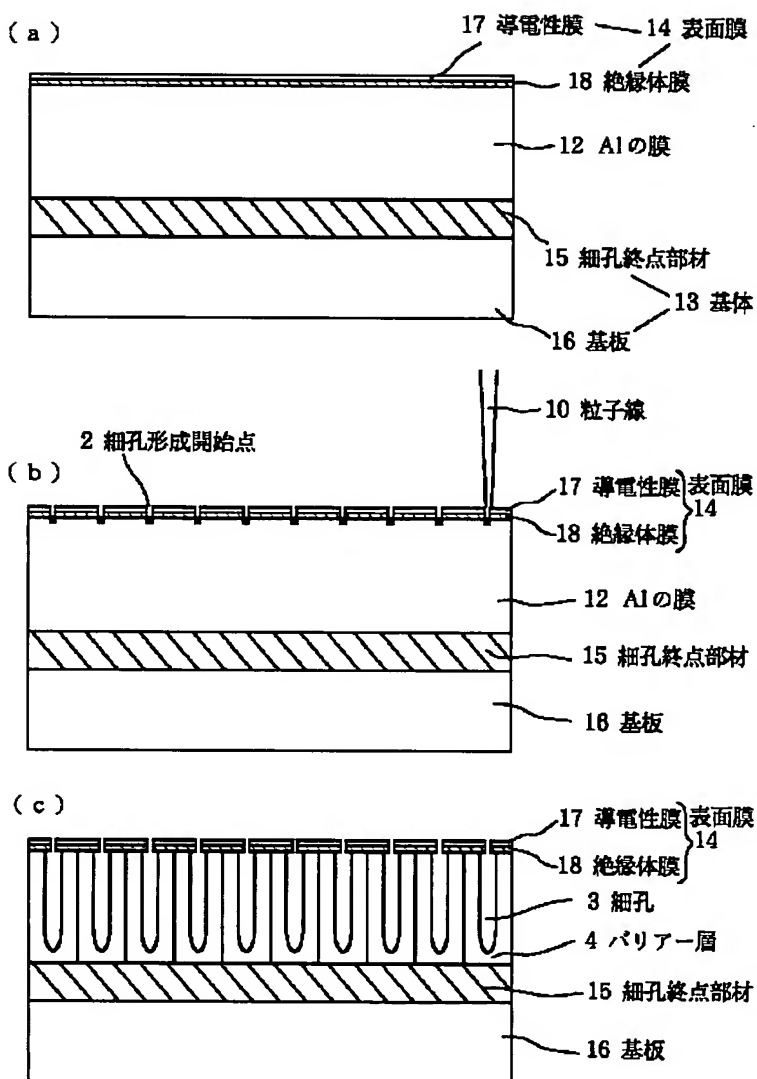


[Drawing 7]

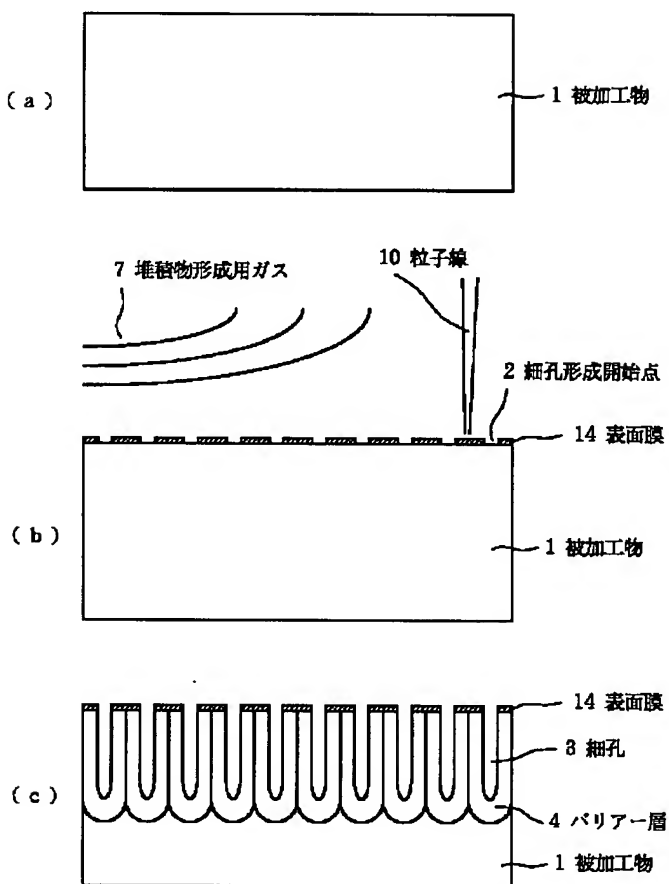




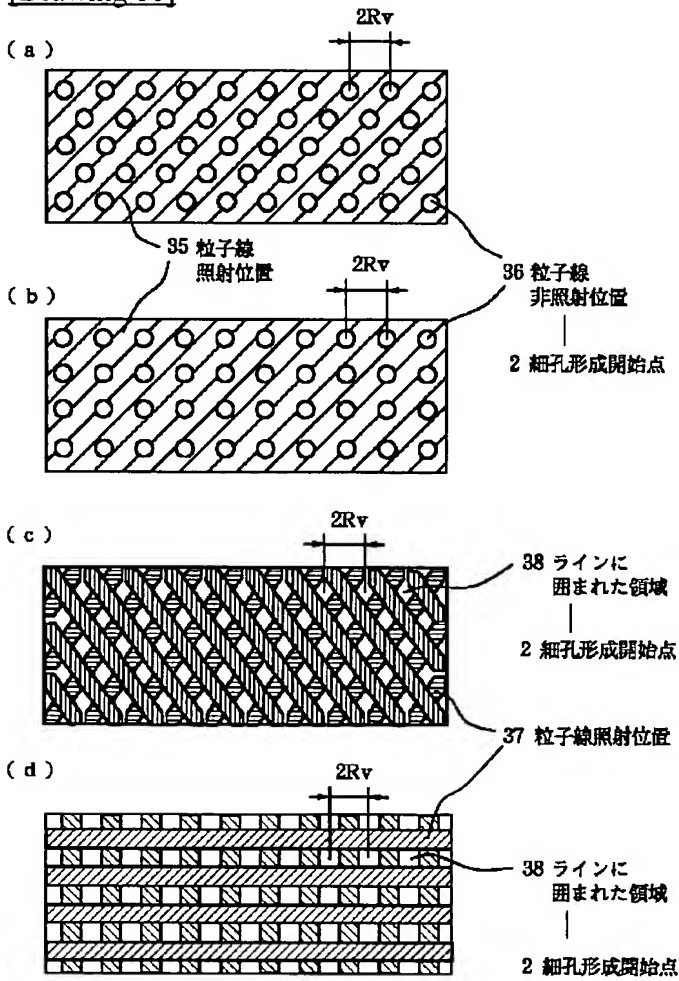
[Drawing 8]



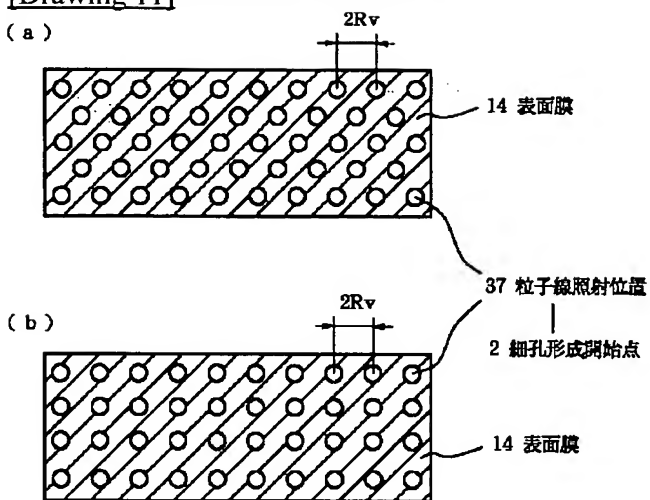
[Drawing 9]



[Drawing 10]



[Drawing 11]



[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号  
特開2001-105400  
(P2001-105400A)

(43) 公開日 平成13年4月17日 (2001.4.17)

(51) Int.Cl. <sup>7</sup>	識別記号	F I	テームコード (参考)
B 8 1 C 5/00		B 8 1 C 5/00	4 E 0 6 6
B 2 3 K 15/00	5 0 8	B 2 3 K 15/00	5 0 8
15/08		15/08	
C 2 5 D 11/16	3 0 1	C 2 5 D 11/16	3 0 1

審査請求 未請求 請求項の数19 O L (全 20 頁)

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(31) 優先権主張番号	特願平11-47539		
(32) 優先日	平成11年2月25日 (1999.2.25)		
(33) 優先権主張国	日本 (J P)		
(31) 優先権主張番号	特願平11-216886		
(32) 優先日	平成11年7月30日 (1999.7.30)		
(33) 優先権主張国	日本 (J P)		

最終頁に続く

(54) 【発明の名称】 細孔の製造方法、並びに該製造方法により製造された細孔および該細孔を有する構造体

(57) 【要約】

【課題】 直線性に優れ、規則正しく配置された細孔、  
該細孔を有する構造体の製造方法を提供する。

【解決手段】 被加工物に粒子線を照射する工程、前記  
粒子線を照射した被加工物を陽極酸化することにより前  
記被加工物に細孔を形成する工程を有する細孔の製造方  
法、及び該細孔を有するナノ構造体の製造方法。

## 【特許請求の範囲】

【請求項 1】 被加工物に粒子線を照射する工程、前記粒子線を照射した被加工物を陽極酸化することにより前記被加工物に細孔を形成する工程を有することを特徴とする細孔の製造方法。

【請求項 2】 前記粒子線が荷電粒子ビームであることを特徴とする請求項 1 に記載の細孔の製造方法。

【請求項 3】 前記粒子線が集束イオンビームあるいは電子ビームであることを特徴とする請求項 1 または 2 に記載の細孔の製造方法。

【請求項 4】 前記粒子線を被加工物の複数の部分に照射することを特徴とする請求項 1 乃至 3 のいずれかの項に記載の細孔の製造方法。

【請求項 5】 前記被加工物の同一部分に、前記粒子線を複数回照射することを特徴とする請求項 1 乃至 3 のいずれかの項に記載の細孔の製造方法。

【請求項 6】 前記被加工物に照射する位置によって、照射する粒子線の量を変えて前記粒子線を照射することを特徴とする請求項 1 乃至 3 のいずれかの項に記載の細孔の製造方法。

【請求項 7】 前記粒子線を照射する工程は、前記被加工物の表面に配置された陽極酸化を抑制する膜に前記粒子線を照射することによって、前記膜を選択的に除去する工程であることを特徴とする請求項 1 乃至 6 のいずれかの項に記載の細孔の製造方法。

【請求項 8】 前記粒子線を照射する工程は、前記被加工物を取り巻く雰囲気中に含まれる原料から、前記被加工物の表面に選択的に陽極酸化を抑制する膜を形成する工程であることを特徴とする請求項 1 乃至 6 のいずれかの項に記載の細孔の製造方法。

【請求項 9】 前記被加工物に照射する粒子線の直径が 500 nm 以下であることを特徴とする請求項 1 乃至 8 のいずれかの項に記載の細孔の製造方法。

【請求項 10】 前記集束イオンビームに用いるイオン種の元素が貴金属以外の元素であることを特徴とする請求項 2 乃至 9 のいずれかの項に記載の細孔の製造方法。

【請求項 11】 前記集束イオンビームに用いるイオン種の元素を、前記被加工物に 1 ppm 以上注入することを特徴とする請求項 10 に記載の細孔の製造方法。

【請求項 12】 前記被加工物が Al を主成分とする部材である請求項 1 乃至 11 のいずれかの項に記載の細孔の製造方法。

【請求項 13】 前記陽極酸化を抑制する膜が絶縁体である請求項 7 乃至 12 のいずれかの項に記載の細孔の製造方法。

【請求項 14】 前記陽極酸化を抑制する膜が Nb、Ti、Ta、Zr、W あるいは Hf を含有する金属である請求項 7 乃至 12 のいずれかの項に記載の細孔の製造方法。

【請求項 15】 前記陽極酸化を抑制する膜が絶縁体膜

及びその上に形成した導電性膜からなる請求項 7 乃至 14 のいずれかの項に記載の細孔の製造方法。

【請求項 16】 前記被加工物を取り巻く雰囲気中に含まれる原料が、金属カルボニル、金属水素化物、金属ハロゲン化物あるいは有機化合物であることを特徴とする請求項 8 乃至 15 のいずれかの項に記載の細孔の製造方法。

【請求項 17】 前記有機化合物が有機金属化合物であることを特徴とする請求項 16 に記載の細孔の製造方法。

10 【請求項 18】 請求項 1 乃至 17 のいずれかの方法により製造した細孔。

【請求項 19】 請求項 1 乃至 17 のいずれかの方法により製造した細孔を有する構造体。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、細孔の製造方法、並びに該製造方法により製造された細孔および該細孔を有する構造体に関し、特に電子デバイスや光デバイス、マイクロデバイスなどの機能材料や、構造材料などとして、広い範囲で利用可能である細孔を有するナノ構造体の製造方法及びナノ構造体に関する。

## 【0002】

【従来の技術】金属及び半導体の薄膜、細線、ドットなどでは、ある特徴的な長さより小さいサイズにおいて、電子の動きが閉じ込められることにより、特異な電気的、光学的、化学的性質を示すことがある。このような観点から、機能性材料として、数 100 nm より微細な構造を有する材料（ナノ構造体）への関心が高まっている。

30 【0003】こうしたナノ構造体の製造方法としては、例えば、フォトリソグラフィーをはじめ、電子線露光、X線露光などの微細パターン形成技術をはじめとする半導体加工技術によって直接的にナノ構造体を製造する方法が挙げられる。

【0004】また、このような製造方法のほかに、自然に形成される規則的な構造、すなわち、自己規則的に形成される構造をベースに、新規なナノ構造体を実現しようとする試みがある。これらの手法は、ベースとして用いる微細構造によっては、従来の方法を上まわる微細で特殊な構造を製造できる可能性があるため、多くの研究が行われ始めている。

【0005】このような自己規則的手法として、ナノサイズの細孔を有するナノ構造体を容易に、制御よく製造することができる陽極酸化が挙げられる。たとえば、アルミニウム及びその合金を酸性浴中で陽極酸化することで製造する陽極酸化アルミナが知られている。

【0006】Al 板を酸性電解質中で陽極酸化すると、多孔質酸化皮膜が形成される（たとえば R. C. Furneaux, W. R. Rigby & A. P. Davids, "NATURE", Vol. 337, P147 (1

989)等参照)。この多孔質酸化皮膜の特徴は、直径が数nm～数百nmの極めて微細な円柱状細孔(ナノホール)が、数nm～数百nmの間隔(セルサイズ)で平行に配列するという特異的な幾何学的構造を有することにある。この円柱状の細孔は、高いアスペクト比を有し、断面の径の一様性にも優れている。またこの細孔の径及び間隔は、陽極酸化の際の電流、電圧を調整することにより、酸化皮膜の厚さ、細孔の深さは陽極酸化の時間を制御することで、ある程度の制御が可能である。

【0007】また細孔の垂直性、直線性及び独立性を改善するために、2段階の陽極酸化を行なう方法、すなわち、陽極酸化を行って形成した多孔質酸化皮膜を一旦除去した後に再び陽極酸化を行なって、より良い垂直性、直線性、独立性を示す細孔を製造する方法が提案されている(“Jpn. Journal of Applied Physics”, Vol. 35, Part 2, No. 1B, pp. L126～L129, 1996年1月15日発行)。ここで、この方法は最初の陽極酸化により形成した陽極酸化皮膜を除去するときに行けるアルミニウム板の表面の窪みが、2度目の陽極酸化の細孔形成開始点となることを用いている。

【0008】さらに、細孔の形状、間隔及びパターンの制御性を改善するために、スタンパーを用いて細孔形成開始点を形成する方法、すなわち、複数の突起を表面に備えた基板をアルミニウム板の表面に押しつけてできる窪みを細孔形成開始点として形成した後に陽極酸化を行なって、より良い形状、間隔及びパターンの制御性を示す細孔を製造する方法も提案されている(特開平10-121292号公報)。

【0009】この陽極酸化アルミナの特異的な幾何学構造に着目した、さまざまな応用が試みられている。益田による解説が詳しいが、以下、応用例を列記する。たとえば、陽極酸化膜の耐摩耗性、耐絶縁性を利用した皮膜としての応用や、皮膜を剥離してのフィルターへの応用がある。さらには、ナノホール内に金属や半導体等を充填する技術や、ナノホールのレプリカ技術を用いることにより、着色、磁気記録媒体、EL発光素子、エレクトロクロミック素子、光学素子、太陽電池、ガスセンサをはじめとするさまざまな応用が試みられている。さらには、量子細線、MIM素子などの量子効果デバイス、ナノホールを化学反応場として用いる分子センサーなど多方面への応用が期待されている(益田“固体物理”、31, 493(1996))。

【0010】

【発明が解決しようとする課題】先に述べた半導体加工技術による直接的なナノ構造体、細孔の製造方法は、歩留まりの悪さや装置のコストが高いなどの問題があり、簡易な手法で再現性よく製造できる手法が望まれている。

【0011】このような観点から陽極酸化の手法は、ナ

ノ構造体、細孔を比較的容易に、制御よく製造することができるので好ましい。

【0012】しかしながら通常の陽極酸化のみで製造される細孔体は、その細孔の形状、パターンを制御する多くの技術が開発されているものの、その制御には限りがあった。陽極酸化における制御としては、陽極酸化電圧で細孔間隔を、時間で細孔の深さを、ポアワイド処理で細孔径を、ある程度制御可能であることが知られている。さらには、細孔の配列を制御した例として、益田らにより、適当な陽極酸化条件のもとで陽極酸化をすることでハニカム状に配列した規則化ナノホールを製造した例が報告されている。ただしこの規則化ナノホールにおいては、製造しうる細孔の間隔には制限があること、長時間の陽極酸化が必要であることなどの課題があった。

【0013】また2段階の陽極酸化を行なう方法においては、細孔の垂直性、直進性及び独立性は改善され、さらに局所的には細孔の間隔及びパターンの制御性の良い部分も存在するが、全体的に見ると細孔の間隔及びパターンは一定ではなく、これらの制御性が良くないという課題があった。

【0014】さらにスタンパーを用いて細孔形成開始点を形成する方法においては、細孔の形状、間隔及びパターンの制御性は改善されるが、以下に述べるような課題があった。

(1) スタンパーを使用しているので、表面に凹凸のある被加工物に対しては、細孔形成開始点を均一に形成することは困難である。

(2) スタンパー使用時に被加工物に圧力をかける必要があるため、機械的強度が強い被加工物に対しては、被加工物が破壊されてしまう危険があるので適用困難である。

【0015】(3) スタンパーによる圧縮を利用しているので、アルミニウム表面に膜が形成されたような被加工物に対しては、表面にアルミニウムを露出させることは困難であるのでスタンプ位置を細孔形成開始点とすることは困難である。

(4) スタンパーの使用時には油圧プレスを用いねばならず、パターンの位置決めを高精度に行なうことは容易ではない。

(5) スタンパーの製造には、例えば電子ビームリソグラフィのような手間のかかる微細加工技術を用いねばならず、均一な高密度の突起を有するスタンパーを欠陥なしに短時間で製造するのは容易ではない。

【0016】本発明の目的はこれらの課題を解決することにある。すなわち、本発明の目的は、陽極酸化により製造される細孔および細孔を有する構造体において、細孔の形状、間隔、パターン、位置、方向等を制御する技術を提供することである。

【0017】同時に本発明では、被加工物の形態、例えば表面凹凸、機械的強度、表面の膜の存在等の制約を受

けずに、かつパターン位置の高精度の制御が可能であり、かつ容易に短時間で製造可能な技術を提供することである。

【0018】さらにはこの技術を適用して製造した細孔を有するナノ構造体をベースとし、新規なナノ構造体、ナノ構造デバイスを開示し、ナノホールを機能材料として多様な方向で使用を可能とすることである。

【0019】

【課題を解決するための手段】そこで、本発明の細孔の製造方法は、被加工物に粒子線を照射する工程と、前記粒子線を照射した被加工物を陽極酸化することにより前記被加工物に細孔を形成する工程とを有することを特徴とする。

【0020】本発明は、また、前記粒子線が、荷電粒子ビームであることをも特徴とする。また、前記粒子線が、集束イオンビームあるいは電子ビームであることをも特徴とする。

【0021】本発明はまた、前記粒子線を照射する工程が、前記被加工物の表面に配置された陽極酸化を抑制する膜に前記粒子線を照射することによって、前記膜を選択的に除去する工程であることを特徴とする。

【0022】本発明はまた、前記粒子線を照射する工程が、前記被加工物を取り巻く雰囲気中に含まれる原料から、前記被加工物の表面に、選択的に、陽極酸化を抑制する膜を形成する工程であることを特徴とする。

【0023】本発明によれば、粒子線を被加工物に照射して所望の位置に細孔形成開始点を形成することができ、その結果、被加工物を陽極酸化することにより前記細孔形成開始点の位置に細孔を形成することができる。このため、本発明によれば、ナノメートルスケールの構造体の細孔の配列、間隔、位置、方向等の制御が可能である。

【0024】同時に本発明の製造方法は、細孔形成開始点の形成に粒子線の照射を用いているので、表面に凹凸のある被加工物に対しても細孔形成開始点を均一性高く形成することが容易である。

【0025】また本発明の製造方法は、細孔形成開始点の形成に粒子線の照射を用いているので、細孔形成開始点を形成するときに被加工物に圧力をかける必要がないので、機械的強度が強くない被加工物に対しても適用可能である。

【0026】また本発明の製造方法は、被加工物表面に膜が形成されたような場合でも、前記膜に粒子線を照射することで、部分的に前記膜を除去し、細孔形成開始点を形成することが可能である。

【0027】また本発明の製造方法は、粒子線照射装置を使用するので、付属の2次電子像観察機能などを用いてパターンの位置決めを高精度に行なうことは容易である。

【0028】さらには、本発明の製造方法は、粒子線照

射装置を使用するので、直描によって細孔形成開始点を形成できる。そのため、スタンパー製造などに必要なレジスト塗布、電子ビーム露光、レジスト除去といったような手間のかかる工程は不必要であり、短時間で細孔形成開始点を形成することが可能である。

【0029】

【発明の実施の形態】以下、主に図1を用いて、本発明の細孔、細孔を有する構造体の製造方法について説明する。図1は本発明のナノ構造体の製造方法の一例を示す工程図である。以下の工程(a)～(c)は、主に図1の(a)～(c)に対応する。

【0030】(a)被加工物の準備

まず、細孔を形成する被加工物1を準備する。本発明が好ましく適用可能な被加工物としては、A1を主成分とする部材が挙げられるが、陽極酸化による細孔形成が可能な材質であれば、特に限定されるものではない。例えば、Si、InPあるいはGaAsを主成分とする部材なども本発明の被加工物として用いることができる。

【0031】本発明が好ましく適用可能な被加工物の形態の例を図3の(a)～(d)に示す。第1の形態の例としては、図3(a)に示すようなA1を主成分とするバルク11が挙げられる。またA1を主成分とするバルク11において、表面に平滑性を持たせるために鏡面研磨加工を行なうことは必ずしも必要ではなく、多少の表面凹凸が存在しても本発明は適用可能である。

【0032】次に第2の形態の例としては、図3の

(b)に示すような基体13上にA1を主成分とする膜12を形成したものも挙げられる。このとき基体13としては、石英ガラスをはじめとする絶縁体基板やシリコンやガリウム砒素をはじめとする半導体基板などの基板や、これらの基板の上に1層以上の膜を形成したものが挙げられる。しかし、A1を主成分とする膜12の陽極酸化による細孔形成に不都合がなければ、基体13の材質、厚さ、機械的強度などは特に限定されるものではない。例えば基体13として基板上にTiやNbなどの細孔形成終点部材の膜を形成したものをいれば、細孔の深さの均一性を上げることも可能になる。またA1を主成分とする膜12の成膜方法は、抵抗加熱蒸着、EB蒸着、スパッタ、CVDをはじめとする任意の成膜方法が適用可能である。またA1を主成分とする膜12において、グレインの存在などに起因する表面凹凸が存在しても本発明は適用可能である。

【0033】次に、第3の形態の例としては、A1を主成分とするバルク11に表面膜14を形成したもの(図3(c))、あるいは基体13にA1を主成分とする膜12を形成したものに表面膜14を形成したもの(図3(d))が挙げられる。このとき表面に形成する表面膜14の材質としては、例えば絶縁体、パルプ金属(Nb、Ti、Ta、Zr、Hfなど)あるいはCなどが挙げられるが、陽極酸化による細孔形成に不都合でない材

質であれば、特に限定されるものではない。

【0034】また表面膜14としては単層の膜のみならず2層以上の膜も挙げられるが、陽極酸化による細孔形成に不都合がなければ、個々の層の材質やその組み合わせなどは特に限定されるものではない。例えば図8

(a)に示すように表面膜14が絶縁体膜18及びその上に形成した導電性膜17である2層膜である被加工物の場合には、製造されたナノ構造体は図8(c)のようになるが、最上面の導電性膜を利用することによって製造されたナノ構造体をマイクロ電子デバイスとして応用することも可能になる。また表面膜14において、グレインの存在などに起因する表面凹凸が存在しても本発明は適用可能である。

【0035】本発明の被加工物の形状としては平滑な板状のものに限らず、曲面を有するもの、表面にある程度の凹凸や段差を有するものなどが挙げられるが、陽極酸化による細孔形成に不都合がなければ、特に限定されるものではない。

【0036】(b)細孔形成開始点の形成工程

上記被加工物1に粒子線10(具体的な例としては集束イオンビームや、電子ビーム)を照射することで、所望の位置に細孔形成開始点2を形成する。

【0037】被加工物への粒子線の照射位置の設定は、粒子線照射装置に付属させた観察手段を用いることにより容易に高精度で行なうことが可能である。

【0038】この観察手段としては、特に、集束イオンビームや電子ビームなどの粒子線を試料上で走査したときに発生する2次電子を検出して走査像を得る方法が挙げられる。この方法では観察時に粒子線を被加工物に照射することになる。しかし、十分に少ない量の粒子線を用いて走査像を得ることで、被加工物のパターンニング位置を設定する際の粒子線照射の影響を実質的に無視することは可能である。

【0039】粒子線の照射位置を移動させる方法としては、粒子線自体をスキャンするなどして照射位置を移動させる方法、被加工物を移動させる方法、あるいはその両者を組み合わせる方法などが挙げられる。ここで粒子線自体を移動させる方法は装置的に合理的であるが、移動可能な距離に制限があるので、大面積かつ高密度に細孔形成開始点を形成したいときには両者を組み合わせる方法が適していると考えられる。また被加工物を移動させる方法についても、高精度の位置制御が可能な試料ステージを用いれば、本発明を適用することは可能である。

【0040】次に本発明の粒子線照射による細孔形成開始点の形成方法の例を、図4、図10、図11を用いて説明する。このとき図4(a)、図4(c)、図10

(a)、図10(c)、図11(a)はほぼハニカム状に細孔形成開始点を形成した例である。また、図4

(b)、図4(d)、図10(b)、図10(d)、図

11(b)はほぼ正4角形状に細孔形成開始点を形成した例である。ここで示す例の他にも様々の例が考えられるが、陽極酸化による細孔形成に不都合がなければ、特に限定されるものではない。

【0041】大きく分けると、本発明の粒子線照射による細孔形成開始点の形成方法には、以下の3つの方法がある。第一の方法は、被加工物表面に粒子線を照射することで、被加工物表面を物理的およびあるいは化学的に変化させる方法である。

【0042】そして、第二の方法は、被加工物表面に形成したマスク(陽極酸化を抑制する膜)に粒子線を照射することで部分的にマスクを除去し、被加工物の表面を部分的に露出させて、そこを細孔形成開始点とする方法である。

【0043】さらに、第三の方法は、被加工物表面に粒子線を照射することで、被加工物を取り巻く雰囲気中存在する原料から、被加工物表面に細孔形成開始点としたい箇所の周りにマスク(陽極酸化を抑制する膜)を形成する方法である。

【0044】まず、第一の方法について説明する。第一の方法には、細孔形成開始点としたい場所のみに、選択的に粒子線を照射する方法と、細孔形成開始点としたい場所以外にも粒子線を照射するが、その照射量の差で、細孔形成開始点を形成する方法とがある。

【0045】上記、細孔形成開始点としたい場所のみに、選択的に、粒子線を照射する方法の例としては、例えば、被加工物にドット(円)状に複数の領域に粒子線を照射する方法(図4(a)、(b))である。図4

(a)、(b)に示す方法では、あるドット位置31に粒子線を滞在させた後に次のドット位置31に移動して粒子線を滞在させることを繰り返し行なう。このようにすることで、粒子線が照射された領域に細孔形成開始点を形成することができる。ここでドット間の移動時に粒子線を止めたくない場合には、ドット間の移動時間をドット位置での滞在時間に比べて非常に短くすることにより、ドット間の移動の際の粒子線照射の影響を実質的になくすることが可能である。

【0046】また、上記粒子線の照射量の差で細孔形成開始点を形成する方法の例としては、例えば、被加工物に粒子線をライン状にそして交点を形成するように照射する方法(図4(c)、(d))がある。この方法は例えば、被加工物に粒子線を異なる方向にライン状に照射することで、少なくとも、2回照射される部分(交点)を形成する。より具体的には、例えば、図4(c)、

(d)に示すように、粒子線を互いに直交するライン32状にスキャンし、1度だけ照射する方法が挙げられる。この方法においては、ラインの交点33においてはその周囲に比べて粒子線が複数回照射されるので、ラインの交点33に細孔形成開始点を形成できる。

【0047】ここで、粒子線を照射した箇所、あるいは



粒子線照射量(回数)の多い箇所が細孔形成開始点になる理由を以下に述べる。粒子線として、集束イオンビームを用いた場合には、イオン注入による化学的な変化(組成変化など)、及びまたは、イオンエッチングによる物理的な変化により、周囲と異なる状態が被加工物表面に形成され、それが陽極酸化の際の特異点(細孔形成開始点)となり陽極酸化が進行すると推定している。

【0048】また、粒子線として、電子線を用いた場合には、電子ビーム照射による熱的な変形、ダメージ発生、蒸発などの物理的な変化、及びまたは化学的な変化(組成変化など)によって、周囲と異なる状態が被加工物表面に形成され、それが陽極酸化の際の特異点(細孔形成開始点)となり陽極酸化が進行すると推定している。

【0049】上記した製造方法は、被加工物の表面に粒子線を照射することで、被加工物に直接、何らかの変化を生じせしめた部位を細孔形成開始点とするものである。しかし、本発明の細孔形成開始点の形成方法は、上記方法に限られるものではない。

【0050】次に、前記した本発明の第二の方法について説明する。この方法は、例えば、図3(c)や図3(d)あるいは図8(a)に示すように被加工物の表面に予め、陽極酸化を抑制する膜(表面膜)14を配置し、この膜の所望の位置にだけ、粒子線を照射し、これによって上記膜を部分的に除去し、被加工物の表面を露出させる(図8(b)、図11(a)、(b))。この方法によって、露出した被加工物の表面を細孔形成開始点とするものである。上記、細孔形成開始点としたい場所のみに粒子線を照射する方法の例としては、例えば、被加工物にドット(円)状に粒子線を照射する方法(図11(a)、(b))が挙げられる。図11(a)、(b)に示す方法では、あるドット位置37に粒子線を滞在させた後に次のドット位置37に移動して粒子線を滞在させることを繰り返し行なう。このようにすることで、粒子線が照射された領域の表面膜14を除去し、被加工物を露出させ、露出した領域を細孔形成開始点とすることができる。ここでドット間の移動時に粒子線を止めたくない場合には、ドット間の移動時間をドット位置での滞在時間に比べて非常に短くすることにより、ドット間の移動の際の粒子線照射の影響を実質的になくすることが可能である。

【0051】次に、前記した本発明の第三の方法について説明する。この方法は、上記第二の方法とは逆に、図9(b)に示す様に、陽極酸化を抑制する膜を形成するための原料を含む雰囲気7中で、被加工物の所望の領域に粒子線を照射することで、被加工物の表面に前記した陽極酸化を抑制する膜14を所望の位置にのみ配置することができる。そして、その結果、粒子線を照射していない被加工物の表面(膜14が形成されていない被加工物の表面)を、細孔形成開始点とすることができる(図

10)。この方法による細孔形成開始点の形成方法の一例として、例えば、細孔形成開始点としたいパターン(図10(a)、(b)ではドット(円)状、図10(c)、(d)では矩形状)を残して、残る被加工物の表面35を粒子線で照射することで、細孔形成開始点を形成することができる。特に、図10(c)、(d)に示したパターンにおいては、被加工物表面に、粒子線をライン状に走査し、ライン状の陽極酸化を抑制する膜を間隔を置いて配置することで、陽極酸化を抑制する膜で囲まれた領域38を細孔形成開始点とすることができる。そのため、簡易に細孔形成開始点を形成することができるので好ましい。

【0052】上記陽極酸化を抑制する膜としては、例えば絶縁体が挙げられるが、被加工物の陽極酸化を抑制することのできる材料であれば導電体でも半導体でも構わない。しかし、陽極酸化を安定に行うためには、導電体を用いる場合には貴金属を除くことが好ましい。

【0053】ここで陽極酸化を抑制する膜を形成するための原料を含む雰囲気中での粒子線の非照射位置が細孔形成開始点になる理由を説明する。粒子線照射位置において、上記原料が、熱分解などにより、粒子線照射位置の被加工物上に膜が形成される。そして形成された膜によって、膜の直下に存在する被加工物への細孔形成が抑制されるために、粒子線非照射位置での細孔の形成(成長)が進行すると推定している。

【0054】上記陽極酸化を抑制する膜を形成するための原料の種類の第1の態様としては、金属を成分として有する材料が挙げられる。例えば、 $W(CO)_6$ 、 $Mo(CO)_6$ のような金属カルボニルや金属有機化合物、 $SiCl_4$ 、 $TiCl_4$ 、 $ZrCl_4$ 、 $TaCl_5$ 、 $MoCl_5$ 、 $WF_6$ などの金属ハロゲン化物、あるいは $SiH_4$ 、 $Si_2H_6$ などのような金属水素化物のガスが挙げられる。

【0055】また、上記陽極酸化を抑制する膜を形成するための原料の種類の第2の態様としては、金属を成分として含まない、有機化合物のガスが挙げられる。例えばビレン、トルニトリルなどの芳香族化合物、メタン、エタンなどの炭化水素化合物、アセトンなどのケトン類などのガスが挙げられる。ただし陽極酸化による細孔形成に不都合がなければ、表面膜形成用ガスの種類は特に制限されるものではない。

【0056】また上記陽極酸化を抑制する膜を形成するための原料の使用法としては、単独で用いること、 $Ar$ 、 $He$ 、 $N_2$ などのガスと混合して用いることなどが挙げられるが、陽極酸化による細孔形成に不都合がなければ特にこれらに限定されるものではない。

【0057】さらに上述した第1の原料を使用した場合には、上記陽極酸化を抑制する膜14は、金属を含む。例えば $W(CO)_6$ を原料として使用した場合には、 $W$ を含む膜が形成される。一方、上述の第2の原料を使用

した場合には、上記陽極酸化を抑制する膜14は、炭素を含む膜となる。ただしこれらの膜中には雰囲気中の他の元素が不純物として含まれる場合がある。

【0058】また、さらに、上記原料として、 $Al(CH_3)_3$ や、 $AlCl_3$ を含む雰囲気7中で、 $Al$ を主成分とする被加工物の所望の領域に粒子線を照射することで、被加工物の表面に $Al$ 膜が形成され、実質的に凹凸の $Al$ が形成される。そのため、 $Al$ の凹部（粒子線を照射していない領域、あるいは粒子線の照射量が少ない領域）を細孔形成開始点とすることもできる。したがって、この場合に $Al$ 膜は実質的に陽極酸化を抑制する膜として作用するとみなすことができる。

【0059】次に、本発明に用いられる粒子線について説明する。本発明における粒子線として集束イオンビームを用いる場合には、そのイオン種としては、液体金属イオン源である、 $Ga$ 、 $Si$ 、 $Ge$ 、 $Cs$ 、 $Nb$ 、 $Cu$ などや、電界電離ガスイオン源である $O$ 、 $N$ 、 $H$ 、 $He$ 、 $Ar$ などが挙げられる。しかし、陽極酸化による細孔形成に不都合がなければ、集束イオンビームのイオン種は特に制限されるものではない。

【0060】ただし実際には扱いやすさ取り扱いやすさなどの理由から、集束イオンビームのイオン種として $Ga$ を使用するのが好ましい。またイオン注入の効果を考慮すると、貴金属のような陽極酸化しにくい元素は、本発明における集束イオンビームのイオン種としては好ましくない場合がある。ただし、前述した陽極酸化を抑制するための膜14を形成するため、あるいは、被加工物表面のイオンエッチングなどの被加工物表面の物理的な変形を行うための場合にはその限りではない。またイオン注入による効果については、イオン種、加速電圧などのプロセス諸条件によって変わってくるが、1ppm以上のイオン種の元素が細孔形成開始点に存在していることが望ましい。

【0061】一方、本発明における粒子線として電子ビームを用いる場合には、そのエネルギーとして、1keV以上10MeV未満のものを用いることが好ましい。したがって、電子の加速電圧としては、数kV～数MV程度のものが挙げられる。しかし、陽極酸化による細孔形成に不都合がなければ、電子ビームのエネルギーおよび加速電圧は特に制限されるものではない。ただし実際に

$$Va = (2Rv - 10) / 2 \quad (式2)$$

【0068】を満たす条件、特に式2から±30%の誤差範囲の中で式2を満たす条件を適用することが好ましい。

【0069】このことは深い細孔、および深い細孔を有する構造体を形成しようとする場合には特に望ましい。一方、形成しようとする被加工物の細孔の深さが浅い場合には、細孔形成開始点の間隔に関して上記条件などから規定される制約は緩やかになる。

【0070】上述したように本発明による細孔形成開始

\*は細孔の形状の再現性などの理由から電子ビームのエネルギーとしては、10keV以上1MeV以下のものを使用することが好ましい。したがって、電子ビームの加速電圧としても、10kV以上1MV以下が好ましい。

【0062】次に細孔形成開始点の配置パターンについて説明する。本発明では、細孔形成開始点を任意の位置に形成することが可能である。また、細孔形成開始点位置の間隔及びパターンについては特に限定されるものではない。ただし実際の応用を考慮すると、ほぼ同一の間隔及びパターンの繰り返しの位置に細孔および、細孔を有するナノ構造体を形成することが要求される場合があり、その場合には細孔形成開始点をほぼ同一の間隔及びパターンの繰り返しとなるように形成することになる。

【0063】このとき陽極酸化による細孔形成において、被加工物として、アルミニウムを主成分とする部材を用いた場合には、細孔のパターンが自己組織化によりほぼハニカム状のパターンの繰り返しになる傾向があるので、あらかじめ細孔形成開始点がほぼハニカム状のパターンの繰り返しになるように形成することが好まし

い。このことは深い細孔を有する構造体を形成しようとする場合には特に望ましい。ただし細孔が浅い場合には上記の自己組織化はまだ起こらないので、細孔形成開始点がほぼ正方形など任意の形状のパターンの繰り返しになるように形成することも可能である。

【0064】また陽極酸化による細孔形成において細孔の間隔は、陽極酸化に用いる電解液の種類と濃度と温度、及び、陽極酸化電圧印加方法、電圧値、時間などのプロセス諸条件である程度制御できる。そのため、あらかじめ細孔形成開始点をプロセス諸条件から予想される細孔の間隔に形成することが好ましい。例えば、経験的に細孔の間隔 $2R$ (nm)と陽極酸化電圧 $Va$ (Volt)の間に

【0065】

【数1】

$$2R = 10 + 2Va \quad (式1)$$

【0066】の関係があるため、細孔形成開始点の最近接距離（間隔） $2Rv$ (nm)と陽極酸化電圧 $Va$ (Volt)の条件として

【0067】

【数2】

$$(式2)$$

点の間隔（ $2Rv$ ）は特に制限されるものではないが、実際の応用を考慮すると、5nm以上1000nm以下が好ましい。

【0071】また、本発明で用いることのできる前述した粒子線の強度分布はほぼガウシアン分布している。そのためとはいえ、各細孔形成開始点に対して照射する粒子線照射領域（すなわち粒子線の直径）は、その隣の細孔形成開始点に照射する粒子線照射領域（すなわち粒子線の直径）と重ならないことが望ましい。したがって

本発明において加工に用いる粒子線の直径としては、細孔形成開始点の間隔以下であることが好ましい。よって加工に用いる粒子線の直径としては、500nm以下のものが好ましい。

#### 【0072】(c) 細孔形成工程

上記細孔形成開始点を形成した被加工物1に陽極酸化処理を行うことで、細孔形成開始点2に細孔3を有する構造体を製造する。

【0073】本工程に用いる陽極酸化装置の概略を図5に示す。図5中、1は被加工物、41は恒温水槽、42はPt板のカソード、43は電解液、44は反応容器、45は陽極酸化電圧を印加する電源、46は陽極酸化電流を測定する電流計である。図では省略してあるが、このほか電圧、電流を自動制御、測定するコンピュータなどが組み込まれている。

【0074】被加工物1およびカソード42は、恒温水槽により温度を一定に保たれた電解液中に配置され、電源より試料、カソード間に電圧を印加することで陽極酸化が行われる。

【0075】陽極酸化に用いる電解液は、たとえば、シュウ酸、りん酸、硫酸、クロム酸溶液などが挙げられるが、陽極酸化による細孔形成に不都合がなければ特に限定されるものではない。また各電解液に応じた陽極酸化電圧、温度などの諸条件は、製造するナノ構造体に応じて、適宜設定することができる。

【0076】さらに上記ナノ構造体を酸溶液（陽極酸化アルミナの場合にはたとえばりん酸溶液）中に浸すポアワイド処理により、適宜、細孔径を広げることができる。酸濃度、処理時間、温度などにより所望の径の細孔を有する構造体とすることができる。

【0077】＜ナノ構造体の構成＞図2に本発明の細孔を有する構造体の構成の一例（陽極酸化アルミナ）を記す。図2(a)は平面図、図2(b)は図2(a)のA-A線における断面図を示す。図2において1は被加工物、3は細孔（ナノホール）、4はバリア層である。

【0078】ここで本発明の構造体について説明する。この構造体は、円柱状の細孔3を有し、それぞれの細孔3は互いに平行かつほぼ等間隔に配置している。細孔3の直径2rは数nm～数百nm、間隔（セルサイズ）2Rは数nm～数百nm程度である。細孔3の間隔、直径は、細孔形成開始点の形成条件や陽極酸化に用いる電解液の濃度と温度、及び、陽極酸化電圧印加方法、電圧値、時間、さらには、その後のポアワイド処理条件などのプロセス諸条件である程度制御することができる。また細孔3の深さd（長さ）は、陽極酸化時間、Alの厚さ等で制御することができ、たとえば10nm～100μmの間である。

【0079】また、本発明の製造方法によれば、図2(b)に示した様に、細孔が途中で止まっている形態だけでなく、図6(c)に示す様に、被加工物を貫通する

細孔を有する構造体とすることもできる。

【0080】さらに上記のナノ構造体をモールドまたはマスクとして、ナノ構造体を作ることもできる。このようなナノ構造体の形成の例としては、細孔を有するナノ構造体をモールドとして用いて細孔の中に金属、半導体等の機能材料を埋め込むことにより、量子細線を形成したり、あるいは貫通細孔を有するナノ構造体を蒸着用マスクとして用いて金属、半導体等の機能材料を蒸着することにより、量子ドットを形成したりすることが挙げられるが、ナノ構造体の形成に不都合がなければ特に限定されるものではない。

【0081】ここで、図7の(c)は細孔3の中に充填材6を埋め込むことにより、量子細線を形成した例を示している。

#### 【0082】

【実施例】以下に実施例をあげて、本発明を説明する。

#### 【0083】実施例1

##### (a) 被加工物の準備

図1(a)に示すように、被加工物として純度99.99%のAl板の表面を過塩素酸とエタノールの混合溶液中での電界研磨により鏡面加工を行なったものを準備した。

##### 【0084】(b) 細孔形成開始点の形成工程

集束イオンビーム加工装置を用い被加工物に集束イオンビーム照射を行ない、図1(b)に示すように被加工物に細孔形成開始点2を形成した。ここで集束イオンビーム加工装置のイオン種はGa、加速電圧は30kVである。

【0085】まず、集束イオンビーム加工装置付属の2次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次にイオンビーム径約30nm、イオン電流約3pAの集束イオンビームを用いて、図4(a)に示すように間隔約100nmでほぼハニカムのパターンを繰り返すようにして被加工物に集束イオンビームをドット状に照射することにより細孔形成開始点の形成を行なった。このとき各ドット位置での集束イオンビームの滞在時間は約10msecであった。

##### 【0086】(c) 細孔の形成工程

図5の陽極酸化装置を用いて被加工物に陽極酸化処理を施し、図1(c)に示すように細孔体を形成した。酸電解液は0.3Mシュウ酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約40Vとした。

【0087】次に被加工物を陽極酸化処理後に5wt%りん酸溶液中に30min間浸すことにより、細孔の径を広げた。

##### 【0088】評価（構造観察）

被加工物をFE-SEM（電界放出走査型電子顕微鏡）にて観察したところ、細孔径は約50nm、細孔間隔は約100nmであり、各細孔はほぼハニカム状のパターンの繰り返しが形成されており、細孔の規則性の高いナ

ノ構造体が形成されているのが確認された。

#### 【0089】実施例2

##### (a) 被加工物の準備

図3(b)に示すように、被加工物として石英基板上に厚さ約200nmのAl膜を抵抗加熱蒸着法にて成膜したものを準備した。

##### 【0090】(b) 細孔形成開始点の形成工程

集束イオンビーム加工装置を用い被加工物に集束イオンビーム照射を行ない、図1(b)に示すように被加工物に細孔形成開始点を形成した。ここで集束イオンビーム加工装置のイオン種はGa、加速電圧は30kVである。まず集束イオンビーム加工装置付属の2次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次に、イオンビーム径約30nm、イオン電流約3pAの集束イオンビームを用いて、図4(b)に示すように間隔約60nmでほぼ正4角形のパターンの繰り返しになるようにして被加工物に集束イオンビームをドット状に照射することにより細孔形成開始点の形成を行なった。このとき各ドット位置での集束イオンビームの滞在時間は約100msecであった。

##### 【0091】(c) 細孔の形成工程

図5の陽極酸化装置を用いて被加工物に陽極酸化処理を施し、図1(c)に示すように細孔体を形成した。酸電解液は0.3M硫酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約25Vとした。

【0092】次に被加工物を陽極酸化処理後に5wt%リン酸溶液中に20min間浸すことにより、細孔の径を広げた。

##### 【0093】評価(構造観察)

被加工物をFE-SEMにて観察したところ、細孔径は約40nm、細孔間隔は約60nmであり、各細孔はほぼ正4角形状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。

#### 【0094】実施例3

##### (a) 被加工物の準備

実施例1と同様な被加工物を準備した。

##### 【0095】(b) 細孔形成開始点の形成工程

集束イオンビーム加工装置を用い被加工物に集束イオンビーム照射を行ない、図1(b)に示すように被加工物に細孔形成開始点を形成した。ここで集束イオンビーム加工装置のイオン種はGa、加速電圧は30kVである。まず集束イオンビーム加工装置付属の2次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次にイオンビーム径約30nm、イオン電流約3pAの集束イオンビームを用いて、図4(c)に示すように間隔約100nmでほぼ平行なラインの繰り返しになるように集束イオンビームをライン状に照射したのちに、先のラインに対して60度異なる方向に間隔約100nmでほぼ平行なラインの繰り返しになるように集束

イオンビームをライン状に照射することにより、各ラインの交点に細孔形成開始点の形成を行なった。このときラインの交点での集束イオンビームの滞在時間の合計が約10msecになるように、スキンスピード及びスキャン回数を調整した。

##### 【0096】(c) 細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図1(c)に示すように細孔体を形成した。酸電解液は0.3Mシュウ酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約50Vとした。

【0097】次に被加工物を陽極酸化処理後に5wt%リン酸溶液中に30min間浸すことにより、細孔の径を広げた。

##### 【0098】評価(構造観察)

被加工物をFE-SEMにて観察したところ、細孔径は約50nm、細孔間隔は約115nmであり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。

#### 【0099】実施例4

##### (a) 被加工物の準備

図8(a)に示すように、Si基板16上に約50nmの細孔終端部材15として使用するTi膜をスパッタ法で成膜して基体13を形成した後に、約500nmのAl膜12を抵抗加熱蒸着法で成膜し、さらに表面膜14として絶縁体膜18である約20nmのSiO<sub>2</sub>膜をスパッタ法で、導電性膜17である約20nmのPt膜をスパッタ法で形成したものを被加工物1として準備した。

##### 【0100】(b) 細孔形成開始点の形成工程

集束イオンビーム加工装置を用い被加工物に集束イオンビーム照射を行ない、図8(b)に示すように被加工物に細孔形成開始点を形成した。ここで集束イオンビーム加工装置のイオン種はGa、加速電圧は30kVである。まず集束イオンビーム加工装置付属の2次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次にイオンビーム径約50nm、イオン電流約60pAの集束イオンビームを用いて、図11(a)に示すように間隔約150nmでほぼハニカムのパターンの繰り返しになるようにして被加工物に集束イオンビームをドット状に照射することにより細孔形成開始点の形成を行なった。このとき各ドット位置での集束イオンビームの滞在時間は約30msecであった。

##### 【0101】(c) 細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、細孔体を形成した。酸電解液は0.3Mリン酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約70Vとした。ここで陽極酸化時において、電流値の減少により陽極酸化が細孔終端部材まで到達したことを確認することができた。

【0102】次に被加工物を陽極酸化処理後に5wt%リン酸溶液中に30min間浸すことにより、細孔の径を広げた(図8(c)参照)。

【0103】評価(構造観察)

被加工物をFE-SEMにて観察したところ、表面膜での細孔径は約50nm、アルミナ膜での細孔径は約70nm、細孔間隔は約150nmであり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。また被加工物の電氣的測定を行なったところ、表面のPt膜は導電性を保持していることと同時に、表面のPt膜と細孔終端部材であるTi膜の間で絶縁されていることが確認された。

【0104】実施例5

本実施例は、細孔を有する部分以外の部分を除去することにより貫通細孔を有するナノ構造体を作製した例である。

【0105】(a)被加工物の準備、(b)細孔形成開始点の形成工程

実施例1の(a)、(b)と同様な方法を用いて、被加工物を準備した後に被加工物に細孔形成開始点を形成した。

【0106】(c)細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図1(c)に示すように細孔体を形成した。酸電解液は0.3Mシュウ酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約40Vとした。

【0107】(d)細孔を有する部分以外の部分の除去工程

細孔を有する部分以外の部分の除去工程を図6(a)～(c)に示す。まず図6(a)に示すようなナノ構造体をHgCl<sub>2</sub>飽和溶液に浸すことにより被加工物のAlのバルク11の部分除去した(図6(b))。次に被加工物を5wt%リン酸溶液中に30min間浸すことによりバリア層4を除去すると同時に細孔の径を広げることによって、貫通細孔5を有するナノ構造体を作製した(図6(c))。

【0108】評価(構造観察)

被加工物をFE-SEMにて観察したところ、細孔径は約50nm、細孔間隔は約100nmであり、各貫通細孔はほぼハニカム状のパターンの繰り返しで形成されており、貫通細孔の規則性の高いナノ構造体が形成されているのが確認された。

【0109】実施例6

本実施例は、陽極酸化によって形成した細孔を有するナノ構造体をモールドとして用い、細孔内に金属を充填してナノ構造体(量子細線)を作製した例である。

【0110】(a)被加工物の準備

図7(a)に示すように、Si基板16上に厚さ約50nmの細孔終端部材15として使用するTi膜をスパッ

タ法で成膜して基体13を形成した後に、さらに厚さ約500nmのAl膜12を抵抗加熱蒸着法で成膜したものを被加工物1として準備した。

【0111】(b)細孔形成開始点の形成工程

各ドット位置での集束イオンビームの滞在時間が約100msecであること以外は、実施例1の(b)と同様な方法を用いて、被加工物に細孔形成開始点を形成した。

【0112】(c)細孔の形成工程

実施例1の(c)と同様な方法を用いて、被加工物に細孔を形成後、細孔の径を広げた(図7(b))。ここで陽極酸化時において、電流値の減少により陽極酸化が細孔終端部材まで到達したことを確認することができた。

【0113】(d)細孔内への金属充填工程

次にNi金属電着を行うことにより、細孔内に充填材6を充填した(図7(c))。Ni充填は、0.14MのNiSO<sub>4</sub>、0.5MのH<sub>3</sub>BO<sub>3</sub>からなる電解液中で、Niの対向電極と共に浸して電着することでナノホール内にNiを析出させた。

20 【0114】評価(構造観察)

Ni充填前の被加工物をFE-SEMにて観察したところ、細孔径は約50nm、細孔間隔は約100nmであり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。また細孔が細孔終端部材まで到達していることが確認され、細孔終端部材を配置することで細孔の長さが制御されていた。

【0115】さらにNi充填後の被加工物をFE-SEMにて観察したところ、細孔はNiで充填されており、太さ約50nmのNiからなる量子細線が形成されていた。

【0116】比較例1

本比較例1は、実施例1において(b)細孔形成開始点の形成工程を行なわなかった以外は、実施例1と同様な方法でナノ構造体を作製した。

【0117】評価(構造観察)

被加工物をFE-SEMにて観察したところ、細孔径は30～50nm、細孔間隔は90～100nmであり、各細孔はランダムに形成されており、細孔の規則性は低かった。

【0118】実施例7

(a)被加工物の準備

図1(a)に示すように、被加工物として純度99.99%のAl板の表面を過塩素酸とエタノールの混合溶液中での電解研磨により鏡面加工を行なったものを準備した。

【0119】(b)細孔形成開始点の形成工程

電子ビーム照射装置を用い被加工物に電子ビーム照射を行ない、図1(b)に示すように被加工物に細孔形成開始点を形成した。ここで電子ビーム照射装置の加速電圧

は 200 kV である。

【0120】まず電子ビーム照射装置付属の 2 次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次にビーム径約 10 nm の電子ビームを用いて、図 4 (a) に示すように間隔 (2 Rv) 約 100 nm でほぼハニカムのパターンの繰り返しになるようにして被加工物に電子ビームをドット状に照射することにより細孔形成開始点の形成を行なった。

【0121】(c) 細孔の形成工程

図 5 の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図 1 (c) に示すように細孔体を形成した。酸電解液は 0.3 M シュウ酸水溶液を用い、恒温水槽により溶液を 3℃ に保持し、陽極酸化電圧は約 40 V とした。

【0122】次に被加工物を陽極酸化処理後、5 wt % リン酸溶液中に 30 min 間浸すことにより、細孔の径を広げた。

【0123】評価 (構造観察)

被加工物を FE-SEM (電界放出走査型電子顕微鏡) にて観察したところ、細孔径は約 50 nm、細孔間隔は約 100 nm であり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。

【0124】実施例 8

(a) 被加工物の準備

図 3 (b) に示すように、被加工物として石英基板 13 上に厚さ約 200 nm の Al 膜 12 を抵抗加熱蒸着法にて成膜したものを準備した。

【0125】(b) 細孔形成開始点の形成工程

電子ビーム照射装置を用い被加工物に電子ビーム照射を行ない、図 1 (b) に示すように被加工物に細孔形成開始点を形成した。ここで電子ビーム照射装置の加速電圧は 200 kV である。まず電子ビーム照射装置付属の 2 次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次にビーム径約 10 nm の電子ビームを用いて、図 4 (b) に示すように間隔 (2 Rv) 約 60 nm でほぼ正 4 角形のパターンの繰り返しになるようにして被加工物に電子ビームをドット状に照射することにより細孔形成開始点の形成を行なった。

【0126】(c) 細孔の形成工程

図 5 の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図 1 (c) に示すように細孔体を形成した。酸電解液は 0.3 M 硫酸水溶液を用い、恒温水槽により溶液を 3℃ に保持し、陽極酸化電圧は約 25 V とした。

【0127】次に被加工物を陽極酸化処理後、5 wt % リン酸溶液中に 20 min 間浸すことにより、細孔の径を広げた。

【0128】評価 (構造観察)

被加工物を FE-SEM にて観察したところ、細孔径は約 40 nm、細孔間隔は約 60 nm であり、各細孔はほぼ正 4 角形状のパターンの繰り返しで形成されており、

細孔の規則性の高いナノ構造体が形成されているのが確認された。

【0129】実施例 9

(a) 被加工物の準備

実施例 7 と同様な被加工物を準備した。

【0130】(b) 細孔形成開始点の形成工程

電子ビーム照射装置を用い被加工物に電子ビーム照射を行ない、図 1 (b) に示すように被加工物に細孔形成開始点を形成した。ここで電子ビーム照射装置の加速電圧は 200 kV である。まず電子ビーム照射装置付属の 2 次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次にビーム径約 30 nm の電子ビームを用いて、図 4 (c) に示すように間隔約 100 nm でほぼ平行なラインの繰り返しになるように電子ビームをライン状に照射したのちに、先のラインに対して 60 度異なる方向に間隔約 100 nm でほぼ平行なラインの繰り返しになるように電子ビームをライン状に照射することにより、各ラインの交点に細孔形成開始点の形成を行なった。

【0131】(c) 細孔の形成工程

図 5 の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図 1 (c) に示すように細孔体を形成した。酸電解液は 0.3 M シュウ酸水溶液を用い、恒温水槽により溶液を 3℃ に保持し、陽極酸化電圧は約 50 V とした。

【0132】次に被加工物を陽極酸化処理後、5 wt % リン酸溶液中に 30 min 間浸すことにより、細孔の径を広げた。

【0133】評価 (構造観察)

被加工物を FE-SEM にて観察したところ、細孔径は約 50 nm、細孔間隔は約 115 nm であり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。

【0134】実施例 10

(a) 被加工物の準備

図 8 (a) に詳細に示すように、Si 基板 16 上に厚さ約 50 nm の細孔終点部材 15 として使用する Ti 膜をスパッタ法で成膜して基体 13 を形成した後に、厚さ約 500 nm の Al 膜 12 を抵抗加熱蒸着法で成膜し、さらに表面膜 14 として絶縁体膜 18 である厚さ約 20 nm の SiO<sub>2</sub> 膜をスパッタ法で、導電性膜 17 である厚さ約 20 nm の Pt 膜をスパッタ法で形成したものを被加工物 1 として準備した。

【0135】(b) 細孔形成開始点の形成工程

電子ビーム照射装置を用い被加工物に電子ビーム照射を行ない、図 8 (b) に示すように被加工物に細孔形成開始点 2 を形成した。ここで電子ビーム照射装置の加速電圧は 200 kV である。まず電子ビーム照射装置付属の 2 次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次にイオンビーム径約 10 nm の電子ビ



ームを用いて、図11(a)に示すように間隔約150nmでほぼハニカムのパターンを繰り返しになるようにして被加工物に電子ビームをドット状に照射することにより細孔形成開始点の形成を行なった。

#### 【0136】(c) 細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、細孔体を形成した。酸電解液は0.3Mリン酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約70Vとした。ここで陽極酸化時において、電流値の減少により陽極酸化が細孔終点部材まで到達したことを確認することができた。

【0137】次に被加工物を陽極酸化処理後、5wt%リン酸溶液中に30min間浸すことにより、細孔の径を広げた(図8(c)参照)。

#### 【0138】評価(構造観察)

被加工物をFE-SEMにて観察したところ、表面膜での細孔径は約50nm、アルミナ膜での細孔径は約70nm、細孔間隔は約150nmであり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。また被加工物の電気的測定を行なったところ、表面のPt膜は導電性を保持していることと同時に、表面のPt膜と細孔終点部材であるTi膜の間に絶縁されていることが確認された。

#### 【0139】実施例11

本実施例は、貫通した細孔を有する構造体を製造した例である。(a)被加工物の準備および(b)細孔形成開始点の形成工程は、実施例7の(a)、(b)と同様な方法を用いた。

#### 【0140】(c) 細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図1(c)に示すように細孔体を形成した。酸電解液は0.3Mシュウ酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約40Vとした。

#### 【0141】(d) 細孔を有する部分以外の部分の除去工程

細孔を有する部分以外の部分の除去工程を図6の(a)~(c)に示す。まず図6(a)に示すようなナノ構造体をH<sub>2</sub>SO<sub>4</sub>飽和溶液に浸すことにより被加工物のAlのバルク11の部分除去した(図6(b))。次に被加工物を5wt%リン酸溶液中に30min間浸すことによりバリア層4を除去すると同時に細孔の径を広げることによって、貫通細孔5を有するナノ構造体を製造した(図6(c))。

#### 【0142】評価(構造観察)

被加工物をFE-SEMにて観察したところ、細孔径は約50nm、細孔間隔は約100nmであり、各貫通細孔はほぼハニカム状のパターンの繰り返しで形成されており、貫通細孔の規則性の高いナノ構造体が形成されているのが確認された。

#### 【0143】実施例12

本実施例は、陽極酸化によって形成したモールドとして細孔内に金属を充填してナノ構造体(量子細線)を製造した例である。

#### 【0144】(a) 被加工物の準備

図7の(a)に詳細に示すように、Si基板16上に厚さ約50nmの細孔終点部材15として使用するTi膜をスパッタ法で成膜して基体13を形成した後に、さらに厚さ約500nmのAl膜12を抵抗加熱蒸着法で成膜したものを被加工物1として準備した。

#### 【0145】(b) 細孔形成開始点の形成工程

実施例7の(b)と同様な方法を用いて、被加工物に細孔形成開始点を形成した。

#### 【0146】(c) 細孔の形成工程

実施例7の(c)と同様な方法を用いて、被加工物に細孔を形成した後、細孔の径を広げた(図7(b))。ここで陽極酸化時において、電流値の減少により陽極酸化が細孔終点部材まで到達したことを確認することができた。

#### 【0147】(d) 細孔内への金属充填工程

次に、Ni金属電着を行うことにより、細孔内に充填材6を充填した(図7(c))。Ni充填は、0.14MのNiSO<sub>4</sub>、0.5MのH<sub>3</sub>BO<sub>3</sub>からなる電解液中で、Niの対向電極と共に浸して電着することでナノホール内にNiを析出させた。

#### 【0148】評価(構造観察)

Ni充填前の被加工物をFE-SEMにて観察したところ、細孔径は約50nm、細孔間隔は約100nmであり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。また細孔が細孔終点部材まで到達していることが確認され、細孔終点部材を配置することで細孔の長さが制御されていた。

【0149】さらにNi充填後の被加工物をFE-SEMにて観察したところ、細孔はNiで充填されており、太さ約50nmのNiからなる量子細線が形成されていた。

#### 【0150】実施例13

#### (a) 被加工物準備

図9(a)に示すように、被加工物として純度99.99%のAl板の表面を過塩素酸とエタノールの混合溶液中での電界研磨により鏡面加工を行なったものを準備した。

#### 【0151】(b) 細孔形成開始点の形成工程

集束イオンビーム加工装置を用い被加工物に集束イオンビーム照射を行ない、図9(b)に示すように被加工物に細孔形成開始点を形成した。ここで集束イオンビーム加工装置のイオン種はGa、加速電圧は30kVである。

#### 【0152】まず集束イオンビーム加工装置付属の2次

電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次に、表面膜形成用ガスとしてピレンガスを集束イオンビーム加工装置内に導入した。さらにイオンビーム径約30nm、イオン電流約3pAの集束イオンビームを用いて、図10(a)に示すように集束イオンビームの非照射位置が間隔約150nmでほぼハニカムのパターンの繰り返しになるように集束イオンビームを照射することにより細孔形成開始点の形成を行なった。このとき集束イオンビームの照射位置にはCを含む表面膜が形成されている。

#### 【0153】(c) 細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図9(c)に示すように細孔体を形成した。酸電解液は0.3Mリン酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約70Vとした。

【0154】次に、被加工物を陽極酸化処理後、5wt%リン酸溶液中に30min間浸すことにより、細孔の径を広げた。

#### 【0155】評価（構造観察）

被加工物をFE-SEM（電界放出走査型電子顕微鏡）にて観察したところ、細孔径は約50nm、細孔間隔は約150nmであり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。

#### 【0156】実施例14

##### (a) 被加工物準備

図3(b)に示すように、被加工物として石英基板13上に約200nmのAl膜12を抵抗加熱蒸着法にて成膜したものを準備した。

##### 【0157】(b) 細孔形成開始点の形成工程

集束イオンビーム加工装置を用い被加工物に集束イオンビーム照射を行ない、図9(b)に示すように被加工物に細孔形成開始点を形成した。ここで集束イオンビーム加工装置のイオン種はGa、加速電圧は30kVである。

【0158】まず、集束イオンビーム加工装置付属の2次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次に、表面膜形成用ガスとしてピレンガスを集束イオンビーム加工装置内に導入した。さらにイオンビーム径約30nm、イオン電流約3pAの集束イオンビームを用いて、図10(b)に示すように集束イオンビームの非照射位置が間隔約150nmでほぼ正4角形のパターンの繰り返しになるように集束イオンビームを照射することにより細孔形成開始点の形成を行なった。このとき集束イオンビームの照射位置にはCを含む表面膜が形成されている。

##### 【0159】(c) 細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図9(c)に示すように細孔体を形成した。酸電解液は0.3Mシュウ酸水溶液を用い、恒温水槽により

溶液を3℃に保持し、陽極酸化電圧は約60Vとした。

【0160】次に被加工物を陽極酸化処理後、5wt%リン酸溶液中に30min間浸すことにより、細孔の径を広げた。

#### 【0161】評価（構造観察）

被加工物をFE-SEMにて観察したところ、細孔径は約50nm、細孔間隔は約150nmであり、各細孔はほぼ正4角形状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。

#### 【0162】実施例15

##### (a) 被加工物準備

実施例13と同様な被加工物を準備した。

##### 【0163】(b) 細孔形成開始点の形成工程

集束イオンビーム加工装置を用い被加工物に集束イオンビーム照射を行ない、図9(b)に示すように被加工物に細孔形成開始点を形成した。ここで集束イオンビーム加工装置のイオン種はGa、加速電圧は30kVである。

【0164】まず、集束イオンビーム加工装置付属の2次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次に表面膜形成用ガスとしてW(CO)<sub>6</sub>ガスを集束イオンビーム加工装置内に導入した。次にイオンビーム径約30nm、イオン電流約3pAの集束イオンビームを用いて、図10(c)に示すように間隔約150nmでほぼ平行なラインの繰り返しになるように集束イオンビームをライン状に照射したのちに、先のラインに対して60度異なる方向に間隔約150nmでほぼ平行なラインの繰り返しになるように集束イオンビームをライン状に照射することにより、各ラインに囲まれた領域に細孔形成開始点の形成を行なった。このとき集束イオンビームの照射位置にはWを含む表面膜が形成されている。

##### 【0165】(c) 細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図9(c)に示すように細孔体を形成した。酸電解液は0.3Mリン酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約80Vとした。

【0166】次に、被加工物を陽極酸化処理後、5wt%リン酸溶液中に30min間浸すことにより、細孔の径を広げた。

#### 【0167】評価（構造観察）

被加工物をFE-SEMにて観察したところ、細孔径は約50nm、細孔間隔は約170nmであり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。

#### 【0168】実施例16

本実施例は、細孔を有する部分以外の部分を除去することにより貫通細孔を有するナノ構造体を製造した例であ



る。

【0169】(a) 被加工物準備、(b) 細孔形成開始点の形成工程

実施例13の(a)、(b)と同様な方法を用いて、被加工物を準備した後に被加工物に細孔形成開始点を形成した。

【0170】(c) 細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図9(c)に示すように細孔体を形成した。酸電解液は0.3Mシュウ酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約70Vとした。

【0171】(d) 細孔を有する部分以外の部分の除去工程

細孔を有する部分以外の部分の除去工程を図6の(a)～(c)に示す。まず図9(c)に示すような被加工物をA rイオンエッチングすることにより表面膜14を除去した(図6の(a))。次に被加工物をH g C l<sub>2</sub>飽和溶液に浸すことにより被加工物のA lのバルク11の部分除去した(図6の(b))。次に被加工物を5wt%リン酸溶液中に30min間浸すことによりバリア層4を除去すると同時に細孔の径を広げることによって、貫通細孔5を有するナノ構造体を製造した(図6の(c))。

【0172】評価(構造観察)

被加工物をF E-S E Mにて観察したところ、細孔径は約50nm、細孔間隔は約150nmであり、各貫通細孔はほぼハニカム状のパターンの繰り返しで形成されており、貫通細孔の規則性の高いナノ構造体が形成されているのが確認された。

【0173】実施例17

本実施例は、陽極酸化によって形成した細孔を有するナノ構造体をモールドとして用いて、細孔内に金属を充填してナノ構造体(量子細線)を製造した例である。

【0174】(a) 被加工物準備

図7の(a)に詳細に示すように、S i基板16上に厚さ約50nmの細孔終端部材15として使用するT i膜をスパッタ法で成膜して基体13を形成した後に、さらに厚さ約500nmのA l膜12を抵抗加熱蒸着法で成膜したものを被加工物1として準備した。

【0175】(b) 細孔形成開始点の形成工程

実施例13の(b)と同様な方法を用いて、被加工物に細孔形成開始点を形成した。

【0176】(c) 細孔の形成工程

実施例13の(c)と同様な方法を用いて、被加工物に細孔を形成後、細孔の径を広げた(図7の(b))。ここで陽極酸化時において、電流値の減少により陽極酸化が細孔終端部材まで到達したことを確認することができた。

【0177】(d) 細孔内への金属充填工程

次にN i金属電着を行うことにより、細孔内に充填材6

を充填した(図7の(c))。N i充填は、0.14M N i S O<sub>4</sub>、0.5MH<sub>3</sub>B O<sub>3</sub>からなる電解液中で、N iの対向電極と共に浸して電着することでナノホール内にN iを析出させた。

【0178】評価(構造観察)

N i充填前の被加工物をF E-S E Mにて観察したところ、細孔径は約50nm、細孔間隔は約150nmであり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。また細孔が細孔終端部材まで到達していることが確認され、細孔終端部材を配置することで細孔の長さが制御されていた。

【0179】さらにN i充填後の被加工物をF E-S E Mにて観察したところ、細孔はN iで充填されており、太さ約50nmのN iからなる量子細線が形成されていた。

【0180】実施例18

(a) 被加工物準備

図9(a)に示すように、被加工物として純度99.99%のA l板の表面を過塩素酸とエタノールの混合溶液中での電界研磨により鏡面加工を行なったものを準備した。

【0181】(b) 細孔形成開始点の形成工程

電子ビーム照射装置を用い被加工物に電子ビーム照射を行ない、図9(b)に示すように被加工物に細孔形成開始点を形成した。ここで電子ビーム照射装置の加速電圧は200kVである。

【0182】まず、電子ビーム照射装置付属の2次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次に表面膜形成用ガスとしてピレンガスを電子ビーム照射装置内に導入した。さらにビーム径約10nmの電子ビームを用いて、図10(a)に示すように電子ビームの非照射位置が間隔約150nmでほぼハニカムのパターンの繰り返しになるように電子ビームを照射することにより細孔形成開始点の形成を行なった。このとき電子ビームの照射位置にはCを含む表面膜が形成されている。

【0183】(c) 細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図9(c)に示すように細孔体を形成した。酸電解液は0.3Mリン酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約70Vとした。

【0184】次に被加工物を陽極酸化処理後、5wt%リン酸溶液中に30min間浸すことにより、細孔の径を広げた。

【0185】評価(構造観察)

被加工物をF E-S E M(電界放出走査型電子顕微鏡)にて観察したところ、細孔径は約50nm、細孔間隔は約150nmであり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナ

ノ構造体が形成されているのが確認された。

#### 【0186】実施例19

##### (a) 被加工物準備

図9(a)に示すように、被加工物として石英基板上に厚さ約200nmのAl膜を抵抗加熱蒸着法にて成膜したものを準備した。

##### 【0187】(b) 細孔形成開始点の形成工程

電子ビーム照射装置を用い被加工物に電子ビーム照射を行ない、図9(b)に示すように被加工物に細孔形成開始点を形成した。ここで電子ビーム照射装置の加速電圧は200kVである。

【0188】まず、電子ビーム照射装置付属の2次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次に表面膜形成用ガスとしてピレンガスを電子ビーム照射装置内に導入した。さらにビーム径約10nmの電子ビームを用いて、図10(b)に示すように電子ビームの非照射位置が間隔約150nmでほぼ正4角形のパターンの繰り返しになるように電子ビームを照射することにより細孔形成開始点の形成を行なった。このとき電子ビームの照射位置にはCを含む表面膜が形成されている。

##### 【0189】(c) 細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図9(c)に示すように細孔体を形成した。酸電解液は0.3Mシュウ酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約60Vとした。

【0190】次に被加工物を陽極酸化処理後、5wt%リン酸溶液中に30min間浸すことにより、細孔の径を広げた。

##### 【0191】評価(構造観察)

被加工物をFE-SEMにて観察したところ、細孔径は約50nm、細孔間隔は約150nmであり、各細孔はほぼ正4角形状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。

#### 【0192】実施例20

##### (a) 被加工物準備

実施例18と同様な被加工物を準備した。

##### 【0193】(b) 細孔形成開始点の形成工程

電子ビーム照射装置を用い被加工物に電子ビーム照射を行ない、図9(b)に示すように被加工物に細孔形成開始点を形成した。ここで電子ビーム照射装置の加速電圧は200kVである。

【0194】まず、電子ビーム照射装置付属の2次電子観察機能を用いて、細孔形成開始点を形成する位置を定めた。次に表面膜形成用ガスとしてW(CO)<sub>6</sub>ガスを電子ビーム照射装置内に導入した。次にビーム径約10nmの電子ビームを用いて、図10(c)に示すように間隔約150nmでほぼ平行なラインの繰り返しになるように電子ビームをライン状に照射したのちに、先のラ

インに対して60度異なる方向に間隔約150nmでほぼ平行なラインの繰り返しになるように電子ビームをライン状に照射することにより、各ラインに囲まれた領域に細孔形成開始点の形成を行なった。このとき電子ビームの照射位置にはWを含む表面膜が形成されている。

##### 【0195】(c) 細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図9(c)に示すように細孔体を形成した。酸電解液は0.3Mリン酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約80Vとした。

【0196】次に被加工物を陽極酸化処理後、5wt%リン酸溶液中に30min間浸すことにより、細孔の径を広げた。

##### 【0197】評価(構造観察)

被加工物をFE-SEMにて観察したところ、細孔径は約50nm、細孔間隔は約170nmであり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。

#### 【0198】実施例21

本実施例は、細孔を有する部分以外の部分を除去することにより貫通細孔を有するナノ構造体を製造した例である。

##### 【0199】(a) 被加工物準備、(b) 細孔形成開始点の形成工程

実施例18の(a)、(b)と同様な方法を用いて、被加工物を準備した後に被加工物に細孔形成開始点を形成した。

##### 【0200】(c) 細孔の形成工程

図5の陽極酸化装置を用い被加工物に陽極酸化処理を施し、図9(c)に示すように細孔体を形成した。酸電解液は0.3Mシュウ酸水溶液を用い、恒温水槽により溶液を3℃に保持し、陽極酸化電圧は約70Vとした。

##### 【0201】(d) 細孔を有する部分以外の部分の除去工程

細孔を有する部分以外の部分の除去工程を図6の(a)～(c)に示す。まず図9(c)に示すような被加工物をArイオンエッチングすることにより表面膜14を除去した(図6の(a))。次に被加工物をH<sub>2</sub>SO<sub>4</sub>飽和溶液に浸すことにより被加工物のAlのバルク11の部分を除去した(図6の(b))。次に被加工物を5wt%リン酸溶液中に30min間浸すことによりバリア層4を除去すると同時に細孔の径を広げることによって、貫通細孔5を有するナノ構造体を製造した(図6の(c))。

##### 【0202】評価(構造観察)

被加工物をFE-SEMにて観察したところ、細孔径は約50nm、細孔間隔は約150nmであり、各貫通細孔はほぼハニカム状のパターンの繰り返しで形成されており、貫通細孔の規則性の高いナノ構造体が形成されて

いるのが確認された。

#### 【0203】実施例2

本実施例は、陽極酸化によって形成した細孔を有するナノ構造体をモールドとして用いて、細孔内に金属を充填してナノ構造体（量子細線）を製造した例である。

#### 【0204】（a）被加工物準備

図7の（a）に詳細に示すように、Si基板16上に厚さ約50nmの細孔終端部材15として使用するTi膜をスパッタ法で成膜して基体13を形成した後に、さらに厚さ約500nmのAl膜12を抵抗加熱蒸着法で成膜したものを被加工物1として準備した。

#### 【0205】（b）細孔形成開始点の形成工程

実施例18の（b）と同様な方法を用いて、被加工物に細孔形成開始点を形成した。

#### 【0206】（c）細孔の形成工程

実施例18の（c）と同様な方法を用いて、被加工物に細孔を形成後、細孔の径を広げた（図7の（b））。ここで陽極酸化時において、電流値の減少により陽極酸化が細孔終端部材まで到達したことを確認することができた。

#### 【0207】（d）細孔内への金属充填工程

次にNi金属電着を行うことにより、細孔内に充填材6を充填した（図7の（c））。Ni充填は、0.14M NiSO<sub>4</sub>、0.5MHBO<sub>3</sub>からなる電解液中で、Niの対向電極と共に浸して電着することでナノホール内にNiを析出させた。

#### 【0208】評価（構造観察）

Ni充填前の被加工物をFE-SEMにて観察したところ、細孔径は約50nm、細孔間隔は約150nmであり、各細孔はほぼハニカム状のパターンの繰り返しで形成されており、細孔の規則性の高いナノ構造体が形成されているのが確認された。また細孔が細孔終端部材まで到達していることが確認され、細孔終端部材を配置することで細孔の長さが制御されていた。

【0209】さらにNi充填後の被加工物をFE-SEMにて観察したところ、細孔はNiで充填されており、太さ約50nmのNiからなる量子細線が形成されていた。

#### 【0210】

【発明の効果】以上説明したように、本発明には以下のような効果がある。

（1）細孔の配列、間隔、位置、方向等の制御が可能であり、直線性に優れた細孔が規則正しく配置された細孔、細孔を有するナノ構造体（陽極酸化アルミナ）を製作することが可能になる。

（2）細孔形成開始点の形成に粒子線照射を用いているので、表面に凹凸のある被加工物に対しても細孔形成開始点を均一性高く形成することができる。

【0211】（3）細孔形成開始点の形成に粒子線照射を用いているので、細孔形成開始点を形成するときに被

加工物に圧力をかける必要がないので、機械的強度が強い被加工物に対しても適用可能である。

（4）被加工物表面に膜が形成されたような場合でも、前記膜に粒子線を照射することで、部分的に前記膜を除去し、細孔形成開始点を形成することが可能である。

【0212】（5）粒子線照射装置を使用するので、付属の2次電子像観察機能などを用いてパターンの位置決めを高精度に行なうことは容易である。

（6）粒子線照射装置を使用するので、直描によって細孔形成開始点を形成できる。そのため、スタンパー製造などに必要なレジスト塗布、電子ビーム露光、レジスト除去といったような手間のかかる工程は不必要であり、短時間で細孔形成開始点を形成することが可能である。

#### 【図面の簡単な説明】

【図1】本発明のナノ構造体の製造方法の一例を示す工程図である。

【図2】本発明のナノ構造体の一例を示す概略図である。

【図3】本発明の被加工物の形態の一例を示す説明図である。

【図4】本発明の粒子線照射による細孔形成開始点の形成の一例を示す説明図である。

【図5】陽極酸化装置を示す概略図である。

【図6】本発明の貫通孔を有するナノ構造体の製造方法の一例を示す工程図である。

【図7】本発明の細孔に充填材を有するナノ構造体の製造方法の一例を示す工程図である。

【図8】本発明のナノ構造体の製造方法の一例を示す工程図である。

【図9】本発明のナノ構造体の製造方法の一例を示す工程図である。

【図10】本発明の粒子線照射による細孔形成開始点の形成の一例を示す説明図である。

【図11】本発明の粒子線照射による細孔形成開始点の形成の一例を示す説明図である。

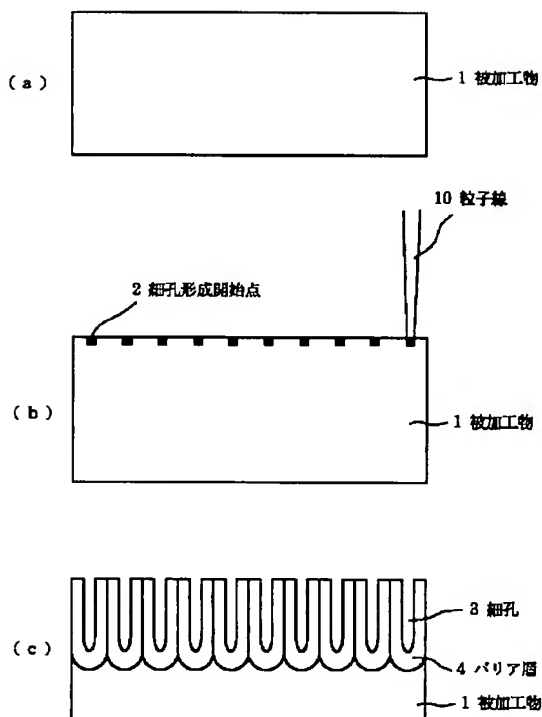
#### 【符号の説明】

- 1 被加工物
- 2 細孔形成開始点
- 3 細孔
- 4 バリア層
- 5 貫通細孔
- 6 充填材
- 10 粒子線
- 11 Alのバルク
- 12 Alの膜
- 13 基体
- 14 表面膜
- 15 細孔終端部材
- 16 基板
- 17 導電性膜

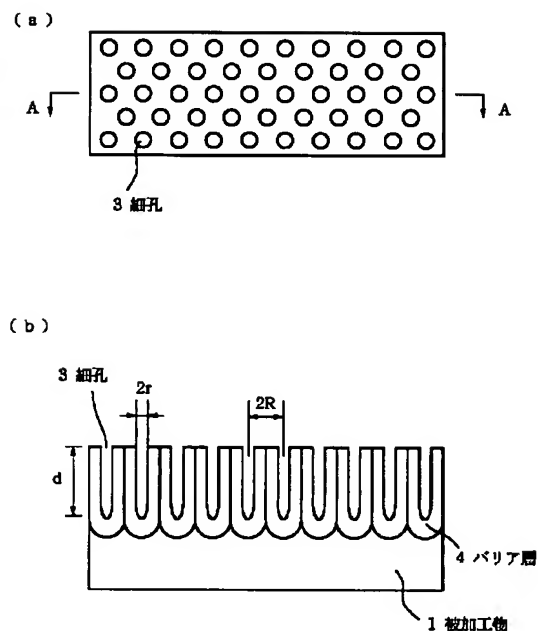
- 18 絶縁体膜  
31 ドット照射位置  
32 ライン照射位置  
33 ライン交点  
41 恒温水槽

- 42 カソード  
43 電解液  
44 反応容器  
45 電源  
46 電流計

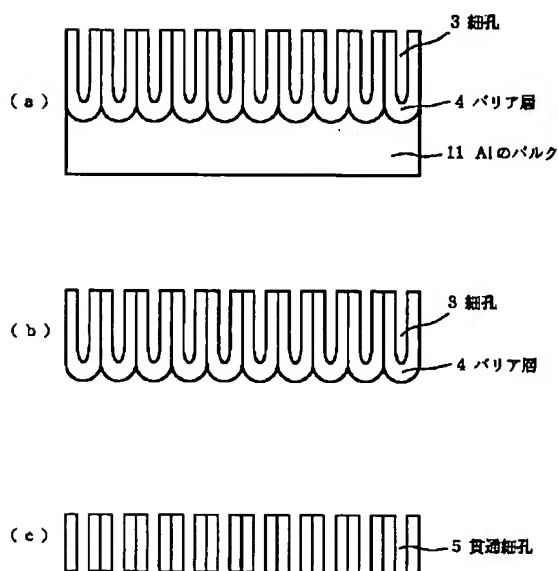
【図1】



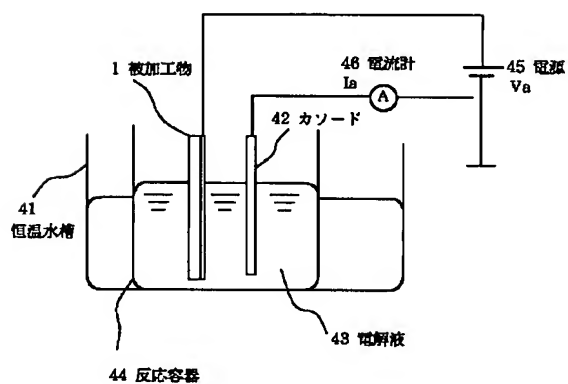
【図2】



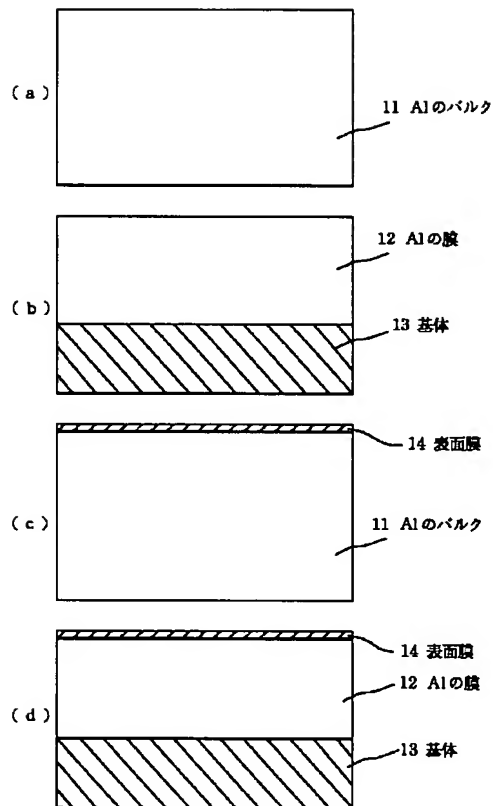
【図6】



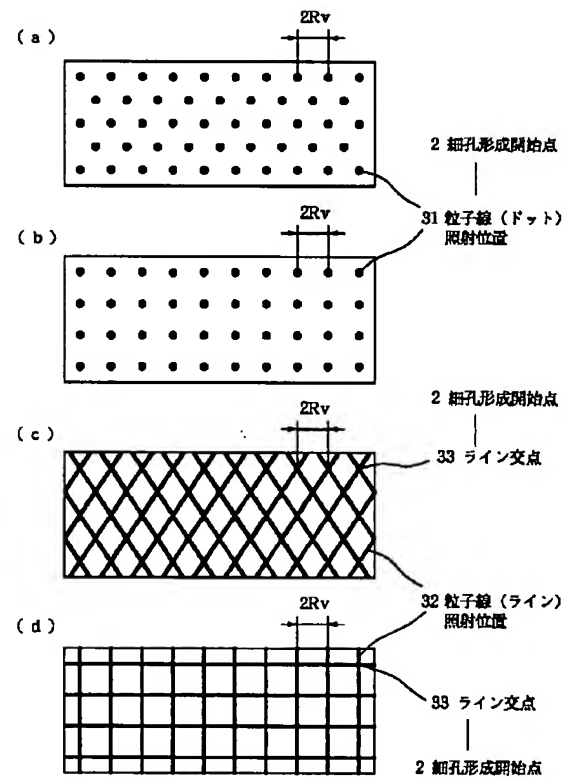
【図5】



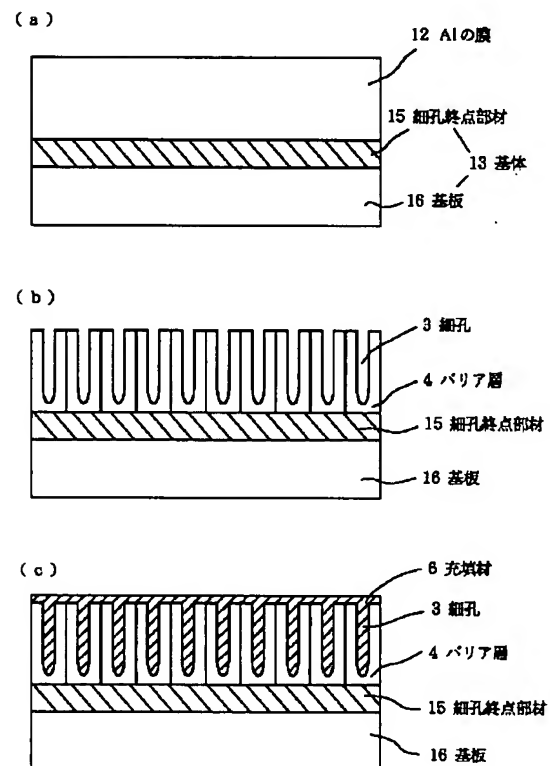
【図3】



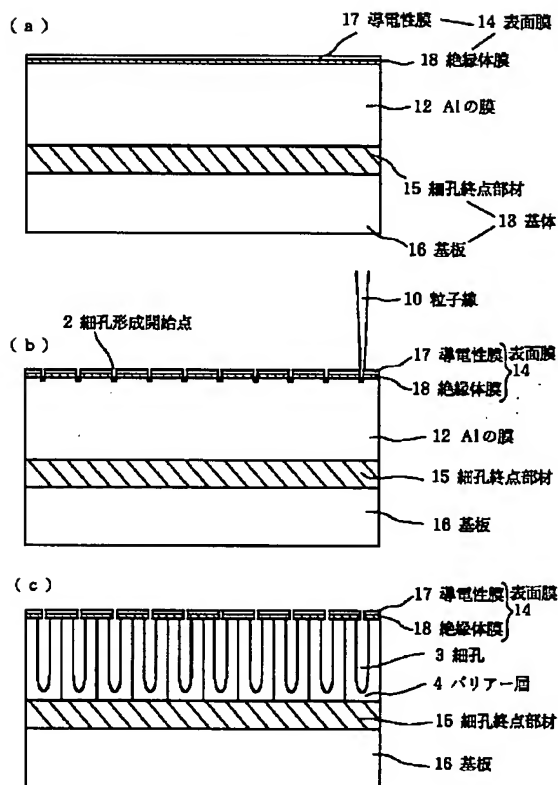
【図4】



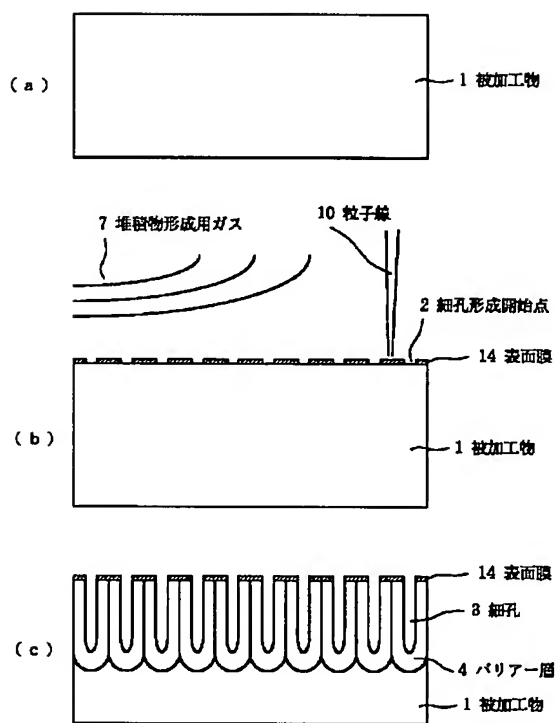
【図7】



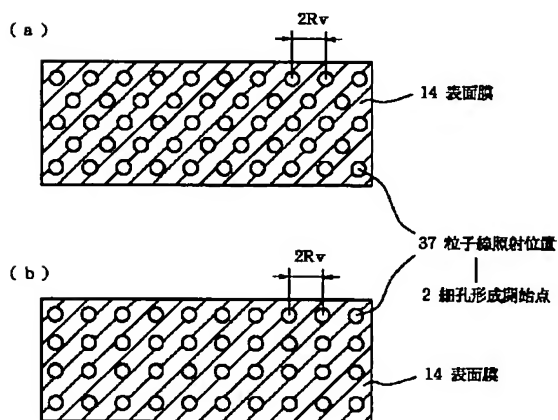
【図8】



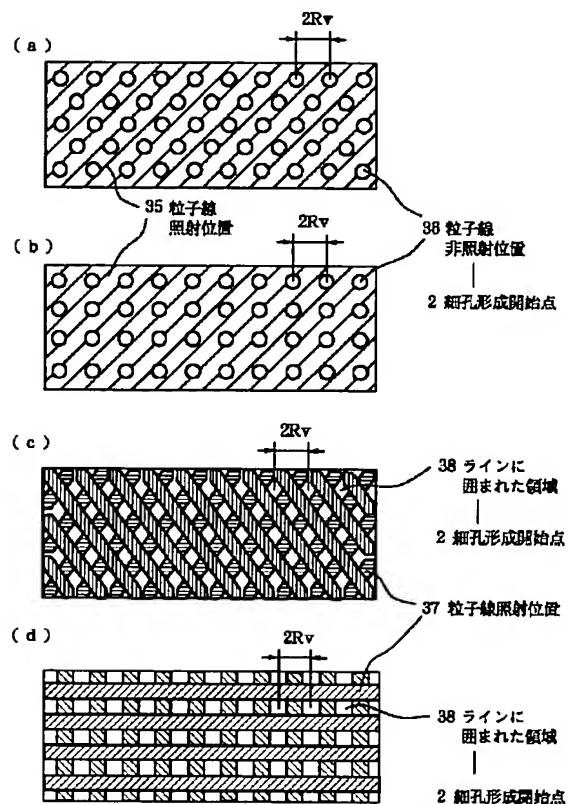
【図9】



【図11】



【図10】



フロントページの続き

(31)優先権主張番号 特願平11-216870

(32)優先日 平成11年7月30日(1999. 7. 30)

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Fターム(参考) 4E066 AA02 BA02 BA06 BA13 BB02  
BC02 CA00 CB10